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Report on Analytical Methodology for Purgeable and Semivolatile Components in Leachates and Solid Wastes

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REPORT ON ANALYTICAL METHODOLOGY FOR PURGEABLE AND SEMIVOLATILE COMPONENTS IN LEACHATES AND SOLID WASTES

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16. ABSTRACT

Two extraction procedures, using tetraglyme and methylene chloride, were developed for the determination of purgeable and semivolatile organic compounds in solid wastes. Extraction efficiencies, method quantification limits and matrix effects were studied for 57 volatile and 142 semivolatile contaminants in a variety of solid waste matrices. Recoveries of spiked compounds were in the 90 to 100% range except for the highly polar materials which could be expected to be poorly recovered. The quantitation limits were found to be 5 µg/g or less for about 90% of the compounds and 1 µg/g or less for half of the compounds. Some significant matrix effects were detected in two matrices. The effects were both compound and matrix dependent and could not be predicted.

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FOREWORD

Environmental measurements are required to determine the quality of ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory - Cincinnati conducts research to:

- Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid wastes.

- Investigate methods for the concentration, recovery, and identification of viruses, bacteria and other microbiological organisms in water; and, to determine the responses of aquatic organisms to water quality.

- Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

- Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This report investigates the analytical behavior of selected organic pollutants in solid wastes and solid waste leachates. Suitable test procedures for their measurement were evaluated and data are presented to demonstrate the applicability of the methods to a variety of waste matrices.

Robert L. Booth

Robert L. Booth, Acting Director
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PREFACE

The U.S. Environmental Protection Agency (EPA) under the Resource Conservation and Recovery Act of 1976 is charged with the responsibility of assessing the potential hazard of municipal and industrial solid wastes. One of the characteristics of a waste that must be determined in order to assess the potential hazard associated with the disposal of the waste is the organic chemical content. In a program recently completed by Battelle's Columbus Laboratories for the EPA Environmental Monitoring Systems Laboratory in Las Vegas under Contract No. 68-03-3098, analytical methodology was evaluated for the determination of individual purgeable and semivolatile organic compounds in solid wastes. As a result of that study, two extraction and gas chromatography-mass spectrometric (GC-MS) analysis methods, one for the determination of purgeable compounds and one for the determination of semivolatile compounds, were developed and applied to a variety of solid wastes in an interlaboratory study. The method for the determination of purgeable compounds involves extraction of the waste with tetraglyme, addition of an aliquot of the extract to water, and analysis by a purge and trap packed column GC-MS procedure. The method for the determination of semivolatile compounds involves extraction of the waste with methylene chloride by sonification under neutral conditions in the presence of anhydrous sodium sulfate added as a drying agent and analysis by a fused silica capillary column GC-MS procedure. The program described in this report was undertaken to provide supporting data related to the application of those two methods to the analysis of solid wastes and solid waste leachates.

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ABSTRACT

This research program was conducted to provide supportive information relating to methods developed previously for the determination of purgeable and semivolatile organic compounds in solid wastes. The effort was comprised of six tasks:

- Task 1. Comparison of solid waste purging methods.
- Task 2. Determination of method quantification limits.
- Task 3. Comparison of solvents for the extraction of semivolatile compounds from solid wastes.
- Task 4. Study of matrix effects on determination of purgeable compounds.
- Task 5. Study of matrix effects on determination of semivolatile compounds.
- Task 6. Comparison of analysis methods for determining purgeable compounds in extracts of solid wastes.

Task 1 was undertaken to determine how well the aqueous dispersion method (3) and the Speis method (2) perform relative to the tetraglyme extraction method (1) for the recovery of purgeable compounds from wastes containing purgeable compounds at levels greater than 1 ppm. The three methods were applied to the analysis of nine types of waste samples using gas chromatography with a photoionization detector and a Hall electrolytic conductivity detector (GC-PID/Hall) as the detection mode. The Speis method gave results that were generally comparable to those obtained by the tetraglyme method but the dispersion method was frequently unsatisfactory.

Task 2 was conducted to determine the quantification limits of the two GC-MS methods for determining 57 representative volatile compounds and 142 representative semivolatile compounds in solid wastes under ideal conditions, i.e. in a clean nonadsorbing matrix. The quantification limit was found to be 5 µg/g or less for about 90 percent of the compounds and 1 µg/g or less for half of the compounds.

Task 3 was conducted to determine whether methyl tert-butyl ether, a halogen-free solvent suitable for total organic halogen (TOX) and gas chromatographic-nitrogen phosphorus detector (GC-NPD) analyses, can be used as a replacement for methylene chloride for the extraction of semivolatile compounds from solid wastes. Six waste samples were extracted using the two solvents. Methyl tert-butyl ether was found to be effective for the extraction of lipophilic wastes, but was significantly less effective than methylene chloride for the extraction of lipophobic wastes.

Task 4 examined whether the extractable nonpurgeable matrix of a waste may sometimes interfere with the purging efficiency of the purgeable compounds when the tetraglyme method is used. Tetraglyme extracts of

nine wastes were analyzed with and without spiking with representative purgeable compounds using GC-PID/Hall analysis and a microcoulimetric purgeable organic halogen (POX) analysis procedure. No matrix effects were found for any of the wastes.

Task 5 was conducted to determine to what extent the total extractable matrix from wastes affect the GC analysis results. Methylene chloride extracts of nine wastes were analyzed with and without spiking with representative semivolatile compounds using GC-FID analysis and a microcoulimetric total organic halogen (TOX) procedure. Very significant matrix effects occurred in the GC analysis of extracts from two of the wastes. The effects were waste dependent and compound dependent. No matrix effects were found in the TOX analyses.

Task 6 was conducted to determine how closely data obtained from GC-PID/Hall analysis and POX analysis agree with data obtained from GC-MS determination of purgeable compounds in extracts of solid wastes. Aqueous leachates and tetraglyme extracts of two solid waste samples were analyzed by GC-MS, GC-PID/Hall, and POX analysis procedures. The three methods gave comparable quantitative results.

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CONCLUSIONS

1. The tetraglyme method for the determination of purgeable compounds in solid wastes is generally comparable to the Speis method in respect to recovery efficiency.

2. The Speis method generally works well for the analysis of solid wastes even when the sample size must be decreased to as little as 2 mg to avoid overloading the detector system.

3. The tetraglyme method and the Speis method are both superior to the aqueous dispersion method.

4. The tetraglyme method is more reproducible than the Speis method.

5. Purgeable organic compounds, especially higher boiling compounds such as bromofluorobenzene, may be irreversibly adsorbed to lipophilic material to a highly variable degree.

6. The quantification limit for the tetraglyme extraction GC-MS analysis method is 0.5 to 5 µg/g for most volatile compounds except those that are highly water soluble.

7. The addition of tetraglyme at a level of four percent to the water in a purge and trap apparatus does not affect the purging efficiency for compounds present at levels as low as 10 µg/L.

8. The quantification limit for the dry neutral extraction GC-MS analysis method is 0.5 to 5 µg/g for most semivolatile compounds including many phenols, anilines, and nitro compounds.

9. Methyl tert-butyl ether is not as effective as methylene chloride for extracting semivolatile compounds from some solid wastes using the dry neutral sonification extraction procedure.

10. Extractable nonpurgeable components present in tetraglyme extracts of solid wastes do not affect the purging efficiency of the purgeable components.

11. Low apparent recoveries, and in some cases high apparent recoveries, of semivolatile compounds spiked into a solid waste can be caused by matrix effects of other extractable components in the GC analysis step instead of by poor or inconsistent extraction efficiencies.

12. There are no significant matrix effects associated with the microcoulimetric procedure for the determination of the POX content or the TOX content of solid waste extracts.

13. The microcoulimetric POX analysis procedure and GC-PID/Hall analysis procedure can be very effective methods for estimating the purgeable organic content of aqueous leachates and tetraglyme extracts obtained from solid wastes. The quantitative data obtained from the two methods in most cases agree within a factor of two with those obtained using a more costly GC-MS analysis procedure.

RECOMMENDATIONS

1. Use either the tetraglyme method or the Speis method, but not the aqueous dispersion method, for the determination of purgeable organic compounds in solid wastes.

2. When using the Speis method, add the internal standards to the organic-free water trap instead of to the sample in order to avoid variable purging efficiencies of the internal standards caused by interaction with the sample.

3. Whenever the reliability of GC or GC-MS analytical data on the semivolatile organic compound content of solid wastes is particularly critical, e.g. when the data are to be used for litigation purposes, analyze spiked extracts as well as spiked samples.

4. Use microcoulimetric POX analysis and GC-PID/Hall analysis for the screening of the purgeable organic content of aqueous leachates and tetraglyme extracts of solid wastes whenever appropriate instead of a more costly GC-MS analysis.

TASK 1. COMPARISON OF SOLID WASTE PURGING METHODS

INTRODUCTION

The tetraglyme extraction method combined with a purge and trap analysis was designed for the determination of volatile organic compounds at levels ranging from 1 ppm to 100% in solid wastes. Two other purge and trap analysis methods, namely the aqueous dispersion method and the Speis method, were designed for the determination of volatile organic compounds at levels ranging from 1 ppb to 1 ppm in aqueous sludges and soils, respectively. All three methods use identical trap, desorb, and analysis procedures and differ only in the sample preparation and purging technique. Task 1 was undertaken to determine how well the aqueous dispersion and the Speis methods perform relative to the tetraglyme extraction method for the analysis of wastes containing high levels (i.e. >1ppm) of volatile compounds.

EXPERIMENTAL

The tetraglyme extraction method (1) involves the extraction of two grams of waste with 40 mL of tetraglyme (tetraethylene glycol dimethyl ether) and addition of 1 to 1000 µL of the extract (representing 0.00005 to 0.05 g of sample) to a purging tube. The Speis method (2) usually involves purging a 2 to 3-gram sample in a sand bath at 80°C and passing the effluent into a purging tube. The Speis method was modified for the comparison study by decreasing the sample size to 0.002 to 1 gram to avoid overloading the GC system. The samples were added directly to the purge vial in the weighing step. No special precautions were taken to avoid loss of volatiles during the weighing of such small samples other than working as quickly as possible. The dispersion method (3) involves diluting a 1 to 5-gram sample with water to give a dispersion containing approximately one percent solid or nonaqueous material and adding the dispersion or an aliquot of the dispersion to a purging tube. Additional dilution was sometimes used in the comparison study to avoid overloading the GC system. For all of the methods the Tenax trap was thermally desorbed and the desorbed effluent was analyzed by GC-PID/Hall analysis in accordance with EPA Methods 601 and 602 (4).

The waste samples used in the comparison study and the sample size represented by the analytical runs for each method are given in Table 1. Different sample sizes were used for different samples to accommodate the different volatile contents of the samples that had been found in the previous study (8). The amounts used for the Speis and dispersion methods were sometimes larger than the amount used for the tetraglyme method to minimize losses in sample handling. The samples assigned ILS numbers are the spiked waste samples that were used in a previous interlaboratory

TABLE 1. SAMPLES USED IN METHODS COMPARISON STUDY

Sample	Sample Size, g, Represented by Analytical Run Using Given Method		
	Tetraglyme	Speis	Dispersion
Spiked Contaminated Soil (ILS-1)	0.05	0.10	0.05
Spiked Latex Paint Waste (ILS-2)	0.001	0.002	0.002
Spiked Spent Ethanes Catalyst (ILS-3)	0.002	0.002	0.002
Spiked Coal Gasification Tar (ILS-4)	0.001	0.002	0.002
Spiked Spent Oxychlorination Catalyst (ILS-5)	0.05	0.20	0.20
Spiked Chemically Treated POTW Sludge (ILS-6)	0.04	0.20	0.10
Oil Refining Waste	0.01	0.05	0.015
Zimpro Sludge	0.05	1.0	0.5
Wet POTW Sludge	0.05	1.0	0.5

study (8). All samples had been homogenized using a Tekmar Tissumizer or a Bramley mill, aliquoted into 30-mL septum-capped vials and allowed to equilibrate at approximately 5°C for at least one week prior to analysis. A Tracor Model 560 gas chromatograph fitted with a Tracor Model 700A Hall electrolytic conductivity detector in series with an HNU photoionization detector was used for the analyses. Each sample was analyzed by each of the three methods in triplicate, i.e. a total of nine aliquots of each sample were weighed out and analyzed. One microgram of 4-bromofluorobenzene (BFB) in 10 µL of methanol was added to the purging tube prior to each analysis to serve as an internal standard.

QUALITY ASSURANCE

A spiked process blank containing 1 µg each of 1,1-dichloroethane, 1,1,1-trichloroethane, 1,2-dichloropropane, bromoform, 1,1,2,2-tetrachloroethane, chlorobenzene, ethylbenzene, o-xylene, and 2-hexanone added as a methanolic spike solution immediately prior to analysis, was run with every six samples. A nonspiked process blank was also run with every six samples. No contamination was detected in any of the nonspiked process blanks at a level of 1 ppm or greater. The spiked process blanks were used as calibration runs to determine the response factors of the components to be quantified. The specific response factors used for the quantification of the compounds detected in a sample run were the average of two response factors, that obtained from the last calibration run before the sample run and that obtained from the first calibration run after the sample run. The response factor calculations were based on the use of 1 µg of 4-bromofluorobenzene (BFB) as an internal standard in all runs. The response factor (RF) of a compound in a calibration run was calculated according to the following equation:

$$RF = \frac{\text{area of BFB}}{\text{area of compound}} \times \frac{\text{µg of compound}}{\text{µg of BFB}}$$

The amount of a compound in a sample run was calculated as follows:

$$\text{µg of compound} = \text{average RF} \times \text{µg of BFB} \times \frac{\text{area of compound}}{\text{area of BFB}}$$

RESULTS AND DISCUSSION

The amount of each analyte found and the percent relative standard deviation from triplicate analyses are given in Tables 2 to 8. No data

TABLE 2. VOLATILE ORGANIC COMPOUNDS IN SPIKED CONTAMINATED SOIL (ILS-1)

Compound	Amount Found, µg/g, Using Given Method (a)		
	Tetraglyme	Speis	Dispersion
1,1,1-Trichloroethane	2(73)	3(63)	1(47)
Bromoform	20(20)	10(38)	7(9)
1,1,2,2-Tetrachloroethane	4(16)	3(45)	< 1
Chlorobenzene	3(40)	2(50)	3(22)
2-Hexanone	7(29)	35(6)	11(32)
Ethylbenzene	11(29)	17(33)	20(52)

(a) The values given are the averages of triplicate determinations with the percent relative standard deviation given in parenthesis.

TABLE 3. VOLATILE ORGANIC COMPOUNDS IN SPIKED LATEX PAINT WASTE (ILS-2)

Compound	Amount Found, µg/g, Using Given Method (a)		
	Tetraglyme	Speis	Dispersion
1,1,1-Trichloroethane	200(19)	660(50)	90(51)
1,2-Dichloropropane	350(64)	110(37)	<5
Bromoform	810(15)	500(59)	420(53)
1,1,2,2-Tetrachloroethane	190(33)	510(71)	190(18)
Chlorobenzene	190(13)	92(25)	110(90)
2-Hexanone	390(14)	120(9)	510(94)
Ethylbenzene	780(4)	360(14)	720(78)
o-Xylene	270(4)	160(15)	290(65)

(a) The values given are the averages of triplicate determinations with the percent relative standard deviation given in parenthesis.

TABLE 4. VOLATILE ORGANIC COMPOUNDS IN SPIKED ETHANES SPENT CATALYST (ILS-3)

Compound	Amount Found, µg/g, Using Given Method (a)		
	Tetraglyme	Speis	Dispersion
1,1-Dichloroethane	8000(10)	8100(2)	2400(16)
1,1,1-Trichloroethane	1900(6)	4100(5)	680(9)
1,2-Dichloropropane	1300(47)	1600(9)	500(4)
Bromoform	1300(6)	1500(27)	920(23)
1,1,2,2-Tetrachloroethane	450(13)	230(26)	330(25)
Chlorobenzene	430(7)	590(25)	130(3)
2-Hexanone	180(12)	430(57)	360(48)
Ethylbenzene	820(9)	1400(10)	400(11)

(a) The values given are the averages of triplicate determinations with the percent relative standard deviation given in parenthesis.

TABLE 5. VOLATILE ORGANIC COMPOUNDS IN SPIKED COAL GASIFICATION TAR (ILS-4)

Compound	Amount Found, µg/g, Using Given Method (a)		
	Tetraglyme	Speis	Dispersion
1,1,1-Trichloroethane	300(11)	190(7)	28(26)
1,2-Dichloropropane	480(81)	600(3)	110(19)
Bromoform	65(14)	160(42)	77(45)
1,1,2,2-Tetrachloroethane	400(14)	1500(21)	490(15)
2-Hexanone	200(45)	1600(27)	<10
Ethylbenzene	100(33)	540(16)	<10
o-Xylene	33(29)	360(9)	<10

(a) The values given are the averages of triplicate determinations with the percent relative standard deviation given in parenthesis.

TABLE 6. VOLATILE ORGANIC COMPOUNDS IN SPIKED SPENT OXYCHLORINATION CATALYST (ILS-5)

Compound	Amount Found, µg/g, Using Given Method (a)		
	Tetraglyme	Speis	Dispersion
1,1,1-Trichloroethane	5(4)	1(59)	<1
Bromoform	3(6)	1	<1
1,1,2,2-Tetrachloroethane	17(17)	9(8)	5(6)
Chlorobenzene	16(20)	3(6)	<1
Ethylbenzene	2(6)	<1	<1
o-Xylene	1(43)	<1	<1

(a) The values given are the averages of triplicate determinations with the percent relative standard deviation given in parenthesis.

TABLE 7. VOLATILE ORGANIC COMPOUNDS IN SPIKED CHEMICALLY TREATED POTW SLUDGE (ILS-9)

Compound	Amount Found, µg/g, Using Given Method (a)		
	Tetraglyme	Speis	Dispersion
1,1-Dichloroethane	1(21)	1(75)	<1
trans 1,2-Dichloroethene	1(23)	1(60)	<1
1,1,1-Trichloroethane	1(7)	1(80)	<1
1,2-Dichloropropane	9(14)	2(5)	<1
1,1,2,2-Tetrachloroethane	1(27)	3(8)	<1
Chlorobenzene	12(5)	10(23)	4(22)
Ethylbenzene	3(9)	8(39)	2(32)

(a) The values given are the averages of triplicate determinations with the percent relative standard deviation given in parenthesis.

TABLE 8. VOLATILE ORGANIC COMPOUNDS IN ZIMPRO SLUDGE

Compound	Amount Found, µg/g, Using Given Method (a)		
	Tetraglyme	Speis	Dispersion
Chlorobenzene	100(51)	19(110)	<1

(a) The values given are the averages of triplicate determinations with the percent relative standard deviation given in parenthesis.

are given from the analysis of the oil refining waste or the wet POTW sludge because no volatile components were detected in these two samples. Only one compound, chlorobenzene, was found in the Zimpro sludge at a level greater than 1 μg/g.

In general, the amounts found using the Speis method were similar to those from the tetraglyme method but the amounts found using the dispersion method were often considerably less than those from the tetraglyme method. The considerably higher levels obtained by the Speis method in the analysis of the coal gasification tar may indicate a significant advantage of the higher purge temperature when the sample is highly lipophilic and not dispersible in water. The precision of the tetraglyme method was somewhat better than that of the other two methods. The average of the percent relative standard deviations of compounds quantified by the tetraglyme method was 22 percent versus 32 percent and 34 percent for the Speis and dispersion methods, respectively. One of the major problems associated with the analyses was the purging efficiency of the BFB used as the internal standard for both the Hall and PID analyses. In the analysis of the Zimpro sludge, the purging efficiency of the BFB was less than 10 percent when the dispersion method was used but greater than 75 percent when either the tetraglyme method or Speis method was used. The BFB may be irreversibly adsorbed by lipophilic material when the dispersion method is used for such a sample.

By using a more volatile internal standard, a higher purging efficiency would undoubtedly be obtained for the internal standard in such samples. This change would improve the accuracy of the values obtained for the more volatile analytes but would seriously decrease the accuracy of the values obtained for the less volatile analytes. On the basis of the Task 1 results, we recommend that only the tetraglyme or the Speis method be used for the determination of volatile components in solid wastes.

TASK 2-1. DETERMINATION OF METHOD QUANTIFICATION LIMITS OF THE TETRAGLYME METHOD

INTRODUCTION

The tetraglyme extraction method (1) was developed as a sample preparation procedure to enable purgeable organic compounds in solid wastes to be determined by GC-MS using a modified EPA Method 624. The method was designed to detect most purgeable components of interest in solid wastes at levels as low as 1 µg/g. The actual quantification limits for various compounds were expected to vary depending upon their response factors and their interaction with the waste matrix. Task 2-1 was conducted to determine the estimated quantification limits of the method for 57 representative volatile compounds under ideal conditions, i.e. under conditions that would avoid any strong interactions between the solid matrix and the representative compounds. The estimated quantification limit was defined for practical purposes for this study as the sample concentration level, which after sample processing and addition of 200 µL of the tetraglyme extract to 5 mL of water in the purging chamber in accordance with the method, would be expected to give a response equivalent to that obtained from 2.5 ng of D_6-benzene added to 5 mL of water in the purging chamber.

EXPERIMENTAL

Selection and Spiking of Sample Matrix

The sample matrix selected for the study was a wet mud prepared from USP grade kaolin and a diatomaceous earth product, Celite 503. The dry powdery solids were heated overnight at 450°C to remove any traces of organic components that might be present. A wet mud was prepared by mixing 50 g of the clay, 50 g of Celite 503, and 125 mL of organic-free water and allowing the mixture to stand overnight to complete the hydration. This mixture simulates a clay soil in many respects, and since it is fully hydrated and organic-free it should not bind small organic molecules.

One-gram aliquots of the above wet mud, in the presence of 20 mL of tetraglyme used as the extraction solvent, were spiked with 57 volatile organic compounds that had been selected for study in the EMSL-Las Vegas sponsored interlaboratory study (8). The compounds are listed in Table 9. Four spike levels, 1, 5, 25, and 125 µg/g, were used. All 57 compounds were used at the two lower spike levels and 31 compounds were used at the two higher levels. Twenty-six of the nonpolar components, those present in Supelco purgeable standards A, B, and C, were deleted from the two higher level standards to minimize the amount of methanol added and to

avoid the necessity for preparing new standards. Since these components were expected to have quantification limits of 5 µg/g or lower, the spiking of these components at higher levels was unnecessary. The total amounts of methanol in the spiking solutions added to the 1-gram aliquots at the 1, 5, 25, and 125 µg/g levels were 0.03, 0.15, 0.38, and 1.88 mL, respectively.

Each spiked aliquot was extracted using the procedure specified for the interlaboratory study. An unspiked aliquot and three replicate spiked aliquots at each of the four spike levels were extracted.

Analysis Procedure

Each tetraglyme extract was analyzed using the purge and trap GC-MS procedure specified for the interlaboratory study.(1) A 200-µL aliquot of the tetraglyme extract was added to a 5-mL purging tube that contained one drop of Antifoam B emulsion and 250 ng of each of four internal standard compounds, D_4-1,2-dichloroethane, D_6-benzene, D_5-ethylbenzene and 4-bromofluorobenzene. The mixture was purged with helium at room temperature for 11 minutes using a flow rate of 40 mL/min. The purged components were trapped on a 25 cm x 2.5 m I.D. stainless steel column packed with 1 cm of 3% OV-1 on 60-80 mesh Chromosorb W, 15 cm of 60-80 mesh Tenax, and 8 cm of 30-60 mesh Davison Grade 15 silica gel. The purgeable components were thermally desorbed by rapidly heating the trap to 180°C and backflushing with helium at a flow rate of 30 mL/min for 4 minutes. The desorbed components were passed directly to a 2 m x 2 mm I.D. glass GC column packed with 1% SP-1000 on 60-80 mesh Carbopack B. The GC column was interfaced with a Finnigan Model 3200 quadrupole mass spectrometer operated with an INCOS data system.

Each of the 57 spiked compounds was searched for and the area response of the selected characteristic ion for each compound was obtained using a computerized search routine. The ratio of the area response obtained for each compound relative to the area response of the characteristic ion of the D_6-benzene, m/e 84, was determined by the computer. The relative retention times and characteristic ions of the compounds are included in Table 9.

QUALITY ASSURANCE

The following quality assurance measures were incorporated into the study:

1. Extractions and analyses of spiked Celite-clay samples were performed in triplicate to permit precision data to be obtained.

TABLE 9. VOLATILE COMPOUNDS USED FOR SPIKING

Compound	Relative Retention Time(a)	Characteristic Ion, m/e
Chloromethane	0.10	50
Bromomethane	0.18	94
Vinyl chloride	0.23	63
Chloroethane	0.29	64
Methylene chloride	0.44	84
Acetone	0.50	58
Dimethyl sulfide	0.48	62
Acrolein	0.50	56
Bromoethane	0.49	108
Acrylonitrile	0.53	53
Carbon disulfide	0.53	76
Propionitrile	0.60	54
2-Chloropropane	0.58	78
Allyl chloride	0.61	76
1,1-Dichloroethylene	0.61	96
trans-1,2-Dichloroethylene	0.72	96
1,1-Dichloroethane	0.67	63
Diethyl ether	0.73	59
Chloroform	0.74	83
1,1,2-Trichlorotrifluoroethane	0.76	101
2-Butanone	0.78	72
1,2-Dichloroethane	0.78	98
Dibromomethane	0.79	93
1,2-Dibromotetrafluoroethane	0.79	179
2-Chloroacrylonitrile	0.81	87
1,1,1-Trichloroethane	0.84	97
Carbon tetrachloride	0.86	117
Epichlorohydrin	0.82	57
Bromodichloromethane	0.89	127
Bis(perfluoroisopropyl)ketone	0.88	69
Methyl acrylate	0.91	55
Dichloroacrylonitrile	0.90	74
Vinyl acetate	0.87	86

TABLE 9. (Continued)

Compound	Relative Retention Time(a)	Characteristic Ion, m/e
1-Chlorobutane	0.93	56
1,2-Dichloropropane	0.95	63
Dimethyl disulfide	0.96	94
trans-1,3-Dichloro-1-propene	0.96	75
Trichloroethylene	0.99	130
Dibromochloromethane	1.02	127
1,1,2-Trichloroethane	1.02	97
cis-1,3-Dichloro-1-propene	0.96	75
Benzene	1.01	78
1,2-Dibromoethane	1.06	107
Fluorobenzene	1.07	96
2-Chloroethyl vinyl ether	1.07	63
Methyl methacrylate	1.12	100
Bromoform	1.14	173
4-Methyl-2-pentanone	1.16	58
2-Hexanone	1.16	58
1,1,2,2-Tetrachloroethane	1.25	83
Tetrachloroethylene	1.25	164
Toluene	1.30	92
Chlorobenzene	1.36	112
Ethylbenzene	1.44	91
Styrene	1.57	104
o-Xylene	1.60	106
m-Bromobenzotrifluoride	1.69	145

(a) Relative to D_6-benzene.

2. An unspiked Celite-clay sample was extracted and analyzed to determine the background levels of components in the sample.

3. The mass spectrometer was tuned each day using 4-bromofluorobenzene to meet the specifications of Budde and Eichelberger (5).

4. The sensitivity of the mass spectrometer was adjusted, by varying the electron multipler voltage, to give an area count of 200,000 to 500,000 for the 250 ng of D_6-benzene added as an internal standard.

5. Each sample was spiked with 250 ng (to give 50 ng/mL) of each of four internal standards, D_4-1,2-dichloroethane, D_6-benzene, D_5-ethylbenzene, and 4-bromofluorobenzene. The retention times and area counts obtained for each compound were monitored to assess the GC-MS performance.

6. Calibration runs containing 200 µL of tetraglyme and 57 purgeable compounds at levels of 10 µg/L and 50 µg/L, which correspond to levels of 5 µg/g and 25 µg/g in the Celite-clay, were analyzed in triplicate to permit the percent recoveries of the compounds from Celite-clay to be calculated.

7. Calibration runs identical to those described above, except that no tetraglyme was added, were analyzed in triplicate to determine the effect of tetraglyme on the purging efficiencies of the compounds.

8. Five blank runs containing 200 µL of tetraglyme but no spike compounds were run, one each day, to establish the range of background levels in the purge and trap system.

RESULTS AND DISCUSSION

The quantification limit for each compound was determined on the basis of the peak area response of the characteristic ion of the compound relative to the response of the characteristic ion of the D_6-benzene added as an internal standard at the 250 ng level, which represents 25 µg/g. The quantification limit was estimated as that concentration that gave a relative peak area of 0.01. Since the area count for the D_6-benzene was usually at least 200,000, a relative peak area of 0.01 represents at least 2,000 counts. Responses of 2,000 area counts are usually reasonably reproducible for the GC-MS system used. Detection limits are usually lower by a factor of 5 to 10 relative to quantification limits estimated

in the above manner; however, the quantitative responses at the lower levels are not sufficiently reproducible to provide reliable quantification.

The peak area ratios obtained at the four spike levels and the estimated quantification limits based on those data are given in Table 10. For 28 of the 57 compounds, the estimated quantification limit was 1 µg/g or less. For another 17 compounds the quantification limit was 2 to 5 µg/g. As expected, the quantification limits were higher for the more polar and more water-soluble compounds. However, even for polar compounds such as acetone, acrylonitrile, propionitrile, 2-butanone, methyl acrylate, dimethyl disulfide, 2-chloroethyl vinyl ether, and 4-methyl-2-pentanone, the estimated quantification limits were 25 µg/g or lower. The only compounds spiked that could not be quantified at the 25 µg/g level were epichlorohydrin, dichloroacrylonitrile, and vinyl acetate.

One of the areas of interest in considering the tetraglyme method is the effect of the tetraglyme on the purging efficiencies of volatile compounds. In order to determine the possible effect of tetraglyme, calibration solutions were analyzed at the 10 µg/L and 50 µg/L levels with and without 4% tetraglyme. The 4% tetraglyme level is that obtained by the addition of 200 µL of tetraglyme to the 5 mL of water in the purging tube. This amount of tetraglyme is the maximum amount that is used in the tetraglyme method. The effect of tetraglyme on relative purging efficiencies is shown in Table 11 which gives the peak area ratios obtained from purging from water and 4% tetraglyme. The results show that tetraglyme at the 4% level has no significant effect on the relative purging efficiency of any of the compounds.

The data presented in Table 11 involve purging efficiencies relative to that of D_6-benzene, one of the internal standards added. The absolute amounts of D_6-benzene and the various compounds purged could be seriously reduced by the addition of tetraglyme without affecting the relative purging efficiencies. However, a check on the absolute area responses obtained for the four internal standards added showed that there was no such reduction in the purged amounts. These absolute area responses are given in Table 12. No significant differences were found between the absolute area responses obtained using distilled water as the purging medium and the responses obtained using 4% tetraglyme.

The percent recoveries obtained for the compounds spiked into Celite and clay at the 5 µg/g and 25 µg/g levels can be determined by comparing the peak area ratios obtained with those obtained from the analysis of the corresponding calibration runs. These data are given in Table 13. The recoveries obtained were 100 $\pm$ 25% in most cases. In a few cases, primarily for the more volatile compounds, the recoveries were

TABLE 10. QUANTIFICATION LIMITS OF THE TETRAGLYME METHOD

Compound	Peak Area Ratio[a] x 1000[b] at Given Concentration, µg/g					Estimated Quantification Limit[c], µg/g
	0	1	5	25	125	
Chloromethane	<5	13(35)	53(6)	NA(d)	NA	1
Bromomethane	11	25(24)	92(21)	NA	NA	0.5
Vinyl chloride	<5	15(20)	67(26)	NA	NA	1
Chloroethane	<5	10(53)	30(18)	NA	NA	1
Methylene chloride	58	860(120)	640(35)	NA	NA	1(e)
Acetone	14	5(71)	11(20)	35(59)	140(16)	10(e)
Dimethyl sulfide	<5	<5	26(9)	140(7)	690(13)	2
Acrolein	62	45(75)	57(53)	75(28)	200(31)	25(e)
Bromoethane	<5	6(33)	32(15)	220(5)	1100(12)	2
Acrylonitrile	10	<5	14(22)	63(8)	410(11)	5
Carbon disulfide	17	73(83)	84(13)	450(5)	2100(5)	1(e)
Propionitrile	<5	<5	<5	21(21)	160(14)	20
2-Chloropropane	<5	<5	<5	10(10)	50(8)	25
Allyl chloride	<5	<5	<5	35(17)	210(8)	10
1,1-Dichloroethylene	<5	10(20)	39(9)	NA	NA	1
trans-1,2-Dichloroethylene	<5	16(35)	59(6)	NA	NA	1
1,1-Dichloroethane	<5	21(49)	70(8)	NA	NA	0.5
Diethyl ether	<5	7(31)	22(7)	110(5)	590(7)	2
Chloroform	74	100(8)	177(2)	NA	NA	1(e)
1,1,2-Trichlorotrifluoroethane	<5	10(16)	43(12)	370(4)	1700(7)	1
2-Butanone	<5	<5	9(1)	24(6)	130(16)	10
1,2-Dichloroethane	<5	<5	6(10)	NA	NA	>5
Dibromomethane	<5	13(8)	70(5)	380(1)	2000(12)	1
1,2-Dibromotetrafluoroethane	<5	20(29)	100(28)	580(24)	2400(33)	0.5
2-Chloroacrylonitrile	<5	7(9)	34(2)	200(2)	1100(7)	2
1,1,1-Trichloroethane	10	21(12)	50(15)	NA	NA	1(e)
Carbon tetrachloride	<5	<5	8(15)	NA	NA	1
Epichlorohydrin	<5	<5	<5	<5	49(19)	50
Bromodichloromethane	<5	<5	<5	NA	NA	>5
Bis(perfluoroisopropyl) ketone	<5	8(7)	37(6)	190(4)	920(2)	2
Methyl acrylate	<5	<5	35(16)	190(14)	1200(2)	2
Dichloroacrylonitrile	<5	<5	<5	<5	<5	>100
Vinyl acetate	<5	<5	<5	<5	47(3)	50
1-Chlorobutane	<5	10(31)	43(8)	230(7)	1100(10)	1
1,2-Dichloropropane	<5	12(5)	66(8)	NA	NA	1
Dimethyl disulfide	<5	<5	<5	31(2)	380(24)	10
trans-1,3-Dichloro-1-propene	<5	<5	24(25)	NA	NA	2
Trichloroethylene	<5	34(35)	130(13)	NA	NA	0.5
Dibromochloromethane	<5	<5	20(18)	NA	NA	4
1,1,2-Trichloroethane	<5	14(4)	67(5)	NA	NA	1
cis-1,3-Dichloro-1-propene	<5	<5	21(66)	NA	NA	4

TABLE 10. (Continued)

Compound	Peak Area Ratio[a] x 1000[b] at Given Concentration, µg/g					Estimated Quantification Limit[c], µg/g
	0	1	5	25	125	
Benzene	32	56(11)	180(5)	NA	NA	0.5(e)
1,2-Dibromoethane	<5	14(4)	80(2)	430(2)	2300(10)	1
Fluorobenzene	<5	40(7)	190(7)	980(1)	4900(4)	0.4
2-Chloroethyl vinyl ether	<5	<5	<5	120(8)	810(7)	5(f)
Methyl methacrylate	<5	<5	11(9)	61(3)	350(10)	5
Bromoform	<5	<5	11(28)	NA	NA	5
4-Methyl-2-pentanone	<5	<5	15(10)	63(13)	410(3)	5
2-Hexanone	<5	<5	14(10)	55(18)	360(4)	5
1,1,2,2-Tetrachloroethane	<5	<5	35(21)	NA	NA	2
Tetrachloroethylene	<5	17(44)	66(23)	NA	NA	1
Toluene	6	29(14)	110(5)	NA	NA	0.5
Chlorobenzene	<5	32(11)	150(9)	NA	NA	0.5
Ethylbenzene	<5	42(4)	190(7)	NA	NA	0.4
Styrene	<5	24(6)	120(9)	610(3)	3000(3)	0.5
o-Xylene	<5	15(10)	73(7)	370(3)	1800(8)	1
m-Bromobenzotrifluoride	<5	17(17)	96(15)	480(10)	2500(17)	1

(a) Peak area ratio obtained for the compound spiked into Celite and clay at the given concentration divided by the peak area obtained for D_6-benzene at a level of 50 µg/L in the purging tube which represents 25 µg/g.

(b) The value given for the peak area ratio x 1000 is the average obtained from triplicate determinations except in the case of the control, 0 µg/g, for which only a single determination was made. The percent relative standard deviation is given in parentheses.

(c) The estimated quantification limit is the concentration level that would be expected to give an average peak area ratio of approximately 0.01, which represents a response equivalent to that obtained from 2.5 ng of D_6-benzene added to the purging chamber.

(d) The compound was not added at this concentration level.

(e) The presence of this compound in the control sample was taken into account in the estimation of the quantification limit.

(f) 2-Chloroethyl vinyl ether could not be quantified at a level of 5 µg/g because of interference from fluorobenzene which coelutes. The response obtained at the 25 µg/g level indicates that 2-chloroethyl vinyl ether would be readily detected at the 5 µg/g level in the absence of interferences.

TABLE 11. EFFECT OF TETRAGLYME ON PURGING EFFICIENCIES

Compound	Peak Area Ratio[a] x 1000 at Given Concentration Using Given Purging Medium				Relative Effect of Tetraglyme at Given Concentration[b]	
	Water		4% Tetraglyme			
	10 µg/L	50 µg/L	10 µg/L	50 µg/L	10 µg/L	50 µg/L
Chloromethane	29(8)	120(38)	22(33)	96(26)	0.8	0.8
Bromomethane	20(12)	340(51)	66(37)	320(20)	1.3	0.9
Vinyl chloride	25(15)	190(61)	29(39)	160(25)	1.2	0.8
Chloroethane	14(14)	110(57)	21(36)	99(24)	1.5	0.9
Methylene chloride	310(14)	1400(32)	400(30)	1900(28)	1.3	1.4
Acetone	11(44)	41(44)	27(50)	43(53)	2.5	1.0
Dimethyl sulfide	13(24)	96(19)	17(43)	92(38)	1.3	1.0
Acrolein	40(18)	54(41)	23(81)	160(25)	0.6	3.0
Bromoethane	14(19)	130(16)	22(27)	110(30)	1.6	0.8
Acrylonitrile	15(15)	74(39)	16(13)	57(59)	1.1	0.8
Carbon disulfide	43(51)	190(15)	48(16)	170(54)	1.1	0.9
Propionitrile	<5	33(49)	<5	25(77)	(c)	0.8
2-Chloropropane	<5	5(11)	<5	5(40)	(c)	1.0
Allyl chloride	<5	26(11)	<5	26(14)	(c)	1.0
1,1-Dichloroethylene	24(11)	120(12)	29(11)	110(73)	1.2	0.9
trans-1,2-Dichloroethylene	43(12)	140(87)	47(9)	240(13)	1.1	1.7
1,1-Dichloroethane	67(12)	310(3)	61(6)	320(1)	0.9	1.0
Diethyl ether	22(11)	89(15)	19(16)	100(5)	0.9	1.1
Chloroform	212(8)	590(11)	220(8)	600(6)	1.0	1.0
1,1,2-Trichlorotrifluoroethane	23(9)	130(20)	26(17)	140(14)	1.1	1.1
2-Butanone	10(12)	32(11)	12(35)	33(21)	1.2	1.0
1,2-Dichloroethane	<5	32(8)	6(17)	35(17)	(c)	1.1
Dibromomethane	67(11)	380(20)	74(16)	390(14)	1.1	1.0
1,2-Dibromotetrafluoroethane	60(24)	440(40)	82(24)	440(22)	1.4	1.0
2-Chloroacrylonitrile	37(10)	200(10)	40(15)	220(15)	1.1	1.1
1,1,2-Trichloroethane	41(15)	200(6)	65(18)	200(5)	1.6	1.0
Carbon tetrachloride	<5	78(3)	10(32)	62(12)	(c)	0.8
Epichlorohydrin	<5	<5	<5	<5	(c)	(c)
Bromodichloromethane	<5	27(19)	<5	24(13)	(c)	0.9
Bis(perfluoroisopropyl) ketone	27(11)	130(6)	29(10)	140(3)	1.1	1.1
Methyl acrylate	41(6)	180(9)	39(23)	210(9)	1.0	1.2
Dichloroacrylonitrile	<5	<5	<5	<5	(c)	(c)
Vinyl acetate	<5	<5	<5	<5	(c)	(c)
1-Chlorobutane	43(1)	160(14)	38(11)	170(15)	0.9	1.1
1,2-Dichloropropane	70(9)	310(12)	61(14)	330(6)	0.9	1.1
Dimethyl disulfide	<5	25(22)	<5	33(15)	(c)	1.3
trans-1,3-Dichloro-1-propene	30(27)	160(5)	26(20)	150(9)	0.9	0.9
Trichloroethylene	67(14)	410(23)	77(14)	420(15)	1.1	1.0
Dibromochloromethane	25(4)	220(21)	27(33)	170(3)	1.1	0.8
1,1,2-Trichloroethane	67(7)	380(19)	75(14)	380(10)	1.1	1.0
cis-1,3-Dichloro-1-propene	24(64)	72(7)	20(69)	91(62)	0.8	1.3

TABLE 11. (Continued)

Compound	Peak Area Ratio[a] x 1000 at Given Concentration Using Given Purging Medium				Relative Effect of Tetraglyme at Given Concentration[b]	
	Water		4% Tetraglyme			
	10 µg/L	50 µg/L	10 µg/L	50 µg/L	10 µg/L	50 µg/L
Benzene	180(2)	760(4)	170(10)	790(5)	0.9	1.0
1,2-Dibromoethane	80(11)	500(25)	91(20)	470(11)	1.1	0.9
Fluorobenzene	180(6)	930(9)	190(5)	960(6)	1.1	1.0
2-Chloroethyl vinyl ether	<5	<5	<5	<5	(c)	(c)
Methyl methacrylate	12(8)	71(11)	12(23)	71(13)	1.0	1.0
Bromoform	15(4)	180(31)	19(74)	130(11)	1.3	0.7
4-Methyl-2-pentanone	17(19)	80(5)	18(41)	73(14)	1.1	0.9
2-Hexanone	17(10)	72(3)	14(40)	69(14)	0.8	1.0
1,1,2,2-Tetrachloroethane	120(12)	660(17)	120(13)	640(15)	1.0	1.0
Tetrachloroethylene	52(18)	340(20)	66(21)	350(15)	1.3	1.0
Toluene	110(2)	550(3)	120(10)	560(2)	1.1	1.0
Chlorobenzene	150(8)	810(12)	160(14)	810(5)	1.1	1.0
Ethylbenzene	180(5)	960(7)	210(21)	980(4)	1.2	1.0
Styrene	120(4)	660(15)	140(31)	640(1)	1.2	1.0
o-Xylene	71(6)	420(24)	90(32)	400(3)	1.3	1.0
m-Bromobenzotrifluoride	80(13)	630(57)	110(30)	520(14)	1.4	0.8

(a) Peak area obtained for the compound at the given concentration divided by the peak area obtained for D_6-benzene at 50 µg/L. The value given is the average of 3 replicates. The percent relative standard deviation is given in parentheses.

(b) Relative effect of tetraglyme = $\frac{\text{Peak area ratio using 4\% tetraglyme}}{\text{Peak area ratio using water}}$

(c) Compound was not detected.

TABLE 12. EFFECT OF TETRAGLYME ON PURGING EFFICIENCY OF INTERNAL STANDARDS

Compound	Area Response Obtained Using Given Purging Medium(b)		Area Response Range Obtained Using Given Purging Medium	
	Distilled Water(c)	4% Tetraglyme(d)	Distilled Water	4% Tetraglyme
D_4-1,2-Dichloroethane	100,000(36)	90,000(26)	45,000-142,000	55,000-140,000
D_6-Benzene	420,000(36)	390,000(28)	177,000-589,000	224,000-639,000
D_5-Ethylbenzene	430,000(34)	390,000(24)	218,000-597,000	245,000-601,000
4-Bromofluorobenzene	200,000(19)	180,000(10)	151,000-256,000	139,000-312,000

(a) Spiked at a level of 50 µg/L in all runs.

(b) The percent relative standard deviation is given in parentheses.

(c) Average of six calibration runs.

(d) Average of 24 runs comprised of 11 calibration runs and 13 runs of extracts of Celite and clay.

TABLE 13. RECOVERY OF PURGEABLE ORGANIC COMPOUNDS FROM SPIKED CELITE AND CLAY

Compound	Peak Area Ratio[a] x 1000[b] from Analysis of Spiked 4% Tetraglyme		Peak Area Ratio[c] x 1000[b] from Analysis of Spiked Celite and Clay		Percent Recovery[f]	
	10 µg/L(d)	50 µg/L(e)	5 µg/g	25 µg/g	5 µg/g	25 µg/g
Chloromethane	22(33)	96(26)	53(6)	NA(g)	240	(h)
Bromomethane	66(37)	320(20)	92(21)	NA	230	(h)
Vinyl chloride	29(39)	160(25)	67(26)	NA	139	(h)
Chloroethane	21(36)	99(24)	30(18)	NA	143	(h)
Methylene chloride	400(30)	1900(28)	640(35)	NA	160	(h)
Acetone	27(50)	43(53)	11(20)	35(59)	41	81
Dimethyl sulfide	17(43)	92(38)	26(9)	140(7)	153	152
Acrolein	23(81)	160(25)	57(53)	75(28)	250	47
Bromoethane	22(27)	110(50)	32(15)	220(5)	145	200
Acrylonitrile	16(13)	57(59)	14(22)	63(8)	88	111
Carbon disulfide	48(16)	170(54)	84(13)	450(5)	175	260
Propionitrile	<5	25(77)	<5	21(12)	(i)	84
2-Chloropropane	<5	5(40)	<5	10(10)	(i)	200
Allyl chloride	<5	26(14)	<5	35(17)	(i)	135
1,1-Dichloroethylene	29(11)	110(73)	39(9)	NA	134	(h)
trans-1,2-Dichloroethylene	47(9)	240(13)	59(6)	NA	126	(h)
1,1-Dichloroethane	61(6)	320(1)	78(8)	NA	115	(h)
Diethyl ether	19(16)	100(5)	22(7)	110(5)	116	110
Chloroform	220(8)	600(6)	177(2)	NA	80	(h)
1,1,2-Trichlorotrifluoroethane	26(17)	140(14)	43(12)	370(4)	165	260
2-Butanone	12(35)	33(21)	9(1)	24(6)	75	73
1,2-Dichloroethane	6(17)	35(17)	6(10)	NA	100	(h)
Dibromomethane	74(16)	390(14)	70(5)	380(1)	95	97
1,2-Dibromotetrafluoroethane	82(24)	440(22)	100(28)	580(24)	122	132
2-Chloroacrylonitrile	40(15)	220(15)	34(2)	200(2)	85	91
1,1,1-Trichloroethane	65(18)	200(5)	50(15)	NA	77	(h)
Carbon tetrachloride	10(32)	62(12)	8(15)	NA	80	(h)
Epichlorohydrin	<5	<5	<5	<5	(i)	(i)
Bromodichloromethane	<5	24(13)	<5	NA	(i)	(h)
Bis(perfluoroisopropyl) ketone	29(10)	140(3)	37(6)	190(4)	128	136
Methyl acrylate	39(23)	210(9)	35(16)	190(14)	90	90
Dichloroacrylonitrile	<5	<5	<5	<5	(i)	(i)
Vinyl acetate	<5	<5	<5	<5	(i)	(i)
1-Chlorobutane	38(11)	170(15)	43(8)	230(7)	113	135

TABLE 13. (Continued)

Compound	Peak Area Ratio[a] x 1000[b] from Analysis of Spiked 4% Tetraglyme		Peak Area Ratio[c] x 1000[b] from Analysis of Spiked Celite and Clay		Percent Recovery[f]	
	10 µg/L[d]	50 µg/L[e]	5 µg/g	25 µg/g	5 µg/g	25 µg/g
1,2-Dichloropropane	61(14)	330(6)	66(8)	NA	108	(h)
Dimethyl disulfide	<5	33(15)	<5	31(2)	(i)	94
trans-1,3-Dichloro-1-propene	26(20)	150(9)	24(25)	NA	92	(h)
Trichloroethylene	77(14)	420(15)	130(12)	NA	169	(h)
Dibromochloromethane	27(33)	170(3)	20(18)	NA	74	(h)
1,1,2-Trichloroethane	75(14)	380(10)	67(5)	NA	89	(h)
cis-1,3-Dichloro-1-propene	20(69)	91(62)	21(66)	NA	105	(h)
Benzene	170(10)	790(5)	180(5)	NA	106	(h)
1,2-Dibromoethane	91(20)	470(11)	80(2)	430(2)	88	91
Fluorobenzene	190(5)	960(6)	190(7)	980(1)	100	102
2-Chloroethyl vinyl ether	<5	<5	<5	120(8)	(i)	(i)
Methyl methacrylate	12(23)	71(13)	11(9)	61(3)	92	86
Bromoform	19(74)	130(11)	11(28)	NA	58	(h)
4-Methyl-2-pentanone	18(41)	73(14)	15(10)	63(13)	83	86
2-Hexanone	14(40)	69(14)	14(10)	55(18)	100	80
1,1,2,2-Tetrachloroethane	120(13)	640(15)	35(21)	NA	29	(h)
Tetrachloroethylene	66(21)	350(15)	66(23)	NA	100	(h)
Toluene	120(10)	560(2)	110(5)	NA	92	(h)
Chlorobenzene	160(14)	810(5)	150(9)	NA	94	(h)
Ethylbenzene	210(21)	980(4)	190(7)	NA	90	(h)
Styrene	140(31)	640(1)	120(9)	610(3)	88	95
o-Xylene	90(32)	400(3)	73(7)	370(3)	81	93
m-Bromobenzotrifluoride	110(30)	520(14)	96(15)	480(10)	87	92

(a) Peak area obtained for the compound spiked into 4% tetraglyme and clay at the given concentration divided by the peak area obtained for D6-benzene at a level of 50 µg/L in the purging tube which represents 25 µg/g.

(b) The value given for the peak area ratio x 1000 is the average obtained from triplicate determinations. The present relative standard deviation is given in parentheses.

(c) Peak area obtained from the compound spiked into Celite and clay at the given concentration divided by the peak area obtained for D_6-benzene at a level of 50 µg/L in the purging tube which represents 25 µg/g.

(d) Corresponds to 5 µg/g of the compound in spiked Celite and clay.

(e) Corresponds to 25 µg/g of the compound in spiked Celite and clay.

(f) Percent Recovery = $\frac{\text{Peak Area Ratio from Analysis of Spiked Celite and Clay}}{\text{Peak Area Ratio from Analysis of Spiked Tetraglyme}} \times 100$

(g) The compound was not added at this concentration level.

(h) Not determined because the compound was not spiked into the Celite and clay at this concentration level.

(i) Not determined because the compound was not detected at this concentration level.

unexplainably high. Possibly some of the more volatile compounds had been lost from the spiking solution used for the calibration runs.

TASK 2-2. DETERMINATION OF METHOD QUANTIFICATION LIMITS OF THE DRY NEUTRAL EXTRACTION METHOD

INTRODUCTION

The dry neutral methylene chloride extraction method (6) was developed as a sample preparation procedure to enable semivolatile organic compounds in solid wastes to be determined by GC-MS using a modified EPA Method 625. The method was designed to detect most semivolatile compounds of interest in solid wastes at levels as low as 1 µg/g. The actual quantification limits for various compounds were expected to vary depending on their response factors and their interaction with the waste matrix. Task 2.2, a parallel study to Task 2-1, was conducted to determine the estimated quantification limits of the method for 142 representative semivolatile compounds under ideal conditions, i.e. under conditions that would avoid any strong interactions between the solid matrix and the representative compounds. The estimated quantification limit was defined for practical purposes for this study as the sample concentration level, which after sample processing and injection of 2 µL of the concentrated extract into the GC in accordance with the method, would be expected to give a response equivalent to that obtained from 0.5 ng of D_{10}-phenanthrene injected onto the GC column.

EXPERIMENTAL

Selection and Spiking of Sample Matrix

The sample matrix selected for the study was a wet mud prepared from USP grade kaolin and a diatomaceous earth product, Celite 503 as described for Task 2-1.

Three-gram aliquots of the above wet mud, in the presence of 150 mL of methylene chloride used as the extraction solvent, were spiked with 142 semivolatile organic compounds that had been selected for study in the EMSL-LV sponsored interlaboratory study. The solutions used for the spiking were those prepared for the interlaboratory study(8). The compounds are listed in Table 14. Four spike levels, 1, 5, 25, and 125 µg/g, were used. All 142 compounds were used at the three lower spike levels and 107 compounds were used at the highest level. Thirty-five of the components, primarily the less soluble compounds, were deleted from the highest level standard to avoid insolubility problems and to avoid the necessity for preparing new standards. Since these components were expected to have quantification limits of 25 µg/g or lower, the spiking of these components at the highest level was unnecessary.

TABLE 14. SEMIVOLATILE COMPOUNDS USED FOR SPIKING

No.	Compound	Relative Retention Time[a]	Characteristic Ion, m/e	No.	Compound	Relative Retention Time[a]	Characteristic Ion, m/e
1	4-Methylpyridine	0.83(1)	93	33	4-Chlorobenzaldehyde	0.92(2)	139
2	1,4-Dichlorobutane	0.93(1)	55	34	2-Nitrophenol	0.92(2)	139
3	Anisole	0.97(1)	108	35	Benzal chloride	0.93(2)	125
4	Bromobenzene	1.01(1)	77	36	2,4-Dimethylphenol	0.95(2)	122
5	2,4-Dimethylpyridine	1.01(1)	107	37	2-Nitrotoluene	0.97(2)	120
6	4-Chlorotoluene	1.08(1)	126	38	Tetralin	0.97(2)	104
7	2-Fluoroaniline	1.09(1)	111	39	Propiophenone	0.97(2)	105
8	Benzaldehyde	1.08(1)	106	40	2,6-Dimethylaniline	0.98(2)	121
9	Thiophenol	1.10(1)	110	41	Benzoic acid	1.00(2)	122
10	Pentachloroethane	1.12(1)	119	42	2,6-Dichlorophenol	0.99(2)	162
11	Aniline	1.13(1)	93	43	1,2,4-Trichlorobenzene	0.99(2)	180
12	Phenol	1.18(1)	94	44	Naphthalene	1.01(2)	128
13	Bis(2-chloroethyl) ether	1.16(1)	93	45	4-Chlorophenol	1.04(2)	128
14	2-Chlorophenol	1.18(1)	128	46	4-Chloroaniline	1.03(2)	127
15	Pentafluorophenol	1.30(1)	184	47	2,4-Dichlorophenol	0.99(2)	162
16	1,2,4-Trimethylbenzene	1.18(1)	105	48	Hexachloropropene	1.03(2)	312
17	2,4,6-Trimethylpyridine	1.19(1)	121	49	4-Nitrotoluene	1.05(2)	137
18	1,4-Dichlorobenzene	1.22(1)	146	50	Hexachlorobutadiene	1.05(2)	225
19	Benzyl chloride	1.23(1)	91	51	Benzotrichloride	1.06(2)	159
20	Benzyl alcohol	0.78(2)	108	52	1-Chloro-4-nitrobenzene	1.08(2)	111
21	1,2-Dichlorobenzene	0.74(2)	146	53	Quinoline	1.08(2)	129
22	2-Methylphenol	0.82(2)	108	54	Bis(2-chloroethoxy)ethane	1.13(2)	63
23	N-Methylaniline	0.83(2)	106	55	4-Chloro-3-methylphenol	0.91(3)	142
24	Acetophenone	0.83(2)	105	56	4-t-Butylphenol	0.91(3)	135
25	4-Methylphenol	0.85(2)	108	57	4-Bromoaniline	0.91(3)	171
26	4-Methylaniline	0.82(2)	107	58	2-Methylnaphthalene	0.91(3)	142
27	Hexachloroethane	0.83(2)	117	59	4-Chloro-2-methylaniline	0.92(3)	141
28	Nitrobenzene	0.86(2)	123	60	4-Chlorobenzoic acid	0.97(3)	139
29	N,N-Dimethylaniline	0.86(2)	120	61	1,2,4,5-Tetrachlorobenzene	0.95(3)	216
30	4-t-Butylpyridine	0.88(2)	120	62	2,4,6-Trichlorophenol	0.98(3)	196
31	1,2,4,5-Tetramethylbenzene	0.90(2)	119	63	2,4,5-Trichlorophenol	0.98(3)	198
32	Decafluorobiphenyl	0.91(2)	265	64	Acetanilide	1.01(3)	93

TABLE 14. (Continued)

No.	Compound	Relative Retention Time[a]	Characteristic Ion, m/e	No.	Compound	Relative Retention Time[a]	Characteristic Ion, m/e
65	2-Chloronaphthalene	1.00(3)	162	98	Diphenylamine	0.90(5)	169
66	Biphenyl	1.00(3)	154	99	Azobenzene	0.90(5)	182
67	1-Chloronaphthalene	1.01(3)	162	100	Trifluralin	0.93(5)	306
68	4-Methylquinoline	1.01(3)	143	101	2-Chloro-4-nitroaniline	0.95(5)	172
69	2-Ethylnaphthalene	1.02(3)	141	102	4-Hydroxybiphenyl	0.96(5)	170
70	Phenyl ether	1.03(3)	170	103	Hexachlorobenzene	0.96(5)	284
71	2-Nitroaniline	1.03(3)	138	104	2,6-Dichloro-4-nitroaniline	0.97(5)	206
72	4-Bromobenzoic acid	1.06(3)	200	105	2,4-Dichlorophenoxyacetic acid	0.97(5)	162
73	3,4-Dichloroaniline	0.95(4)	161	106	4-Aminobiphenyl	0.98(5)	169
74	2-Chloro-4-nitrophenol	0.98(4)	173	107	Pentachlorophenol	0.99(5)	266
75	Acenaphthylene	0.97(4)	152	108	3,3'-Dichlorobiphenyl	0.99(5)	222
76	2,3-Dimethylnaphthalene	0.96(4)	156	109	Pentachloronitrobenzene	1.00(5)	237
77	1,3-Dinitrobenzene	0.97(4)	168	110	Phenanthrene	1.00(5)	178
78	Dimethyl phthalate	0.98(4)	163	111	4,4'-Dichlorobiphenyl	1.00(5)	222
79	2,6-Dinitrotoluene	0.98(4)	138	112	Anthracene	1.01(5)	178
80	3-Nitroaniline	1.00(4)	138	113	Acridine	1.02(5)	179
81	Acenaphthene	1.01(4)	154	114	Phenanthridine	1.03(5)	179
82	2,4-Di-t-butylphenol	1.02(2)	191	115	Carbazole	1.04(5)	167
83	2,4-Dinitrophenol	1.02(4)	184	116	2,4,5-Trichlorophenoxyacetic acid	1.07(5)	196
84	2-Naphthol	1.03(4)	144	117	Di-n-butyl phthalate	0.92(6)	149
85	2,6-Di-t-butyl-4-methylphenol	1.02(2)	205	118	2,4-Dinitroaniline	0.92(6)	183
86	Dibenzofuran	1.03(4)	168	119	2,2',4,4'-Tetrachlorobiphenyl	0.92(6)	292
87	4-Nitrophenol	1.03(4)	109	120	Anthraquinone	0.93(6)	208
88	Pentachlorobenzene	1.04(4)	250	121	Fluoranthene	0.98(6)	202
89	2,4-Dinitrotoluene	1.05(4)	165	122	2,2',4,4',6,6'-Hexachlorobiphenyl	0.99(6)	360
90	1-Aminonaphthalene	1.05(4)	143	123	2-Methylanthraquinone	1.00(6)	222
91	2,4,5-Trichloroaniline	1.05(4)	195	124	Pyrene	1.00(6)	202
92	2,4-Dinitrochlorobenzene	1.07(4)	202	125	4,4'-DDE	0.90(7)	246
93	Fluorene	1.09(4)	166	126	4,4'-DDD	0.93(7)	235
94	4-Chlorophenyl phenyl ether	1.10(4)	204	127	Diethylstilbestrol	0.96(7)	268
95	4-Chloro-2-nitroaniline	1.10(4)	172	128	4,4'-DDT	0.96(7)	235
96	4-Nitroaniline	1.11(4)	138	129	Triphenyl phosphate	0.97(7)	326
97	2-Methyl-4,6-dinitrophenol	1.11(4)	198	130	Benzo(a)anthracene	1.00(7)	228

TABLE 14. (Continued)

No.	Compound	Relative Retention Time[a]	Characteristic Ion, m/e	No.	Compound	Relative Retention Time[a]	Characteristic Ion, m/e
131	Methoxychlor	1.00(7)	227	137	Benzo(k)fluoranthene	0.98(8)	252
132	3,3'-Dichlorobenzidine	1.00(7)	252	138	Benzo(a)pyrene	1.00(8)	252
133	Chrysene	1.00(7)	228	139	Dibenzocarbazole	1.10(8)	267
134	Bis(2-ethylhexyl) phthalate	1.02(7)	149	140	Indeno(1,2,3-cd)pyrene	1.13(8)	276
135	Tri-(tolyl) phosphate	0.96(8)	368	141	Dibenzo(a,h)anthracene	1.13(8)	278
136	Bis(2-ethylhexyl) sebacate	0.97(8)	185	142	Benzo(g,h,i)perylene	1.16(8)	276

(a) Relative to deuterated standard indicated by number in parentheses; 1=D_5-bromobenzene; 2=D_8-naphthalene; 3=D_{10}-biphenyl; 4=D_{10}-acenaphthene; 5=D_{10}-phenanthrene; 6=D_{10}-pyrene; 7=D_{12}-chrysene; 8=D_{12}-benzo(a)pyrene.

Extraction and Analysis Procedure

Each spiked aliquot was extracted using the procedure specified for the interlaboratory study (6). An unspiked aliquot and three replicate spiked aliquots at each of the four spike levels were extracted. Each methylene chloride extract was analyzed using the GC-MS procedure specified for the interlaboratory study. A 100-mL aliquot of each extract was concentrated to 1 mL and a 1-μL aliquot was injected into a GC-MS system fitted with splitless injector and a 30-m x 0.25 mm I.D. DB-5 fused silica capillary column. A Finnigan Model 3200 quadrupole mass spectrometer operated with a INCOS data system was used for this work.

Each of the 142 spiked compounds was searched for and the area response of the selected characteristic ion for each compound was obtained using a computerized search routine. The ratio of the area response obtained for each compound relative to the area response of the characteristic ion of D_{10}-phenanthrene, m/e 188, was determined by the computer. The relative retention times and characteristic ions of the compounds are included in Table 14.

QUALITY ASSURANCE

The following quality assurance measures were incorporated into study:

1. Extractions and analyses of spiked Celite-clay samples were performed in triplicate to permit precision data to be obtained.

2. An unspiked Celite-clay sample was extracted and analyzed to determine the background levels of components attributable to the sample and the extraction system.

3. The mass spectrometer was tuned each day using decafluoro-triphenylphosphine to meet the specification of Eichelberger, et al.

4. The sensitivity of the mass spectrometer was adjusted, by varying the electron multiplier voltage, to give an area count of 200,000 to 500,000 for the 50 ng of D_{10}-phenanthrene injected as an internal standard.

5. Each concentrated extract was spiked with 50 ng/μL of each of 12 internal standards, D_5-bromobenzene, D_8-naphthalene, D_{10}-biphenyl, D_{10}-acenaphthene, D_{10}-phenanthrene, D_{10}-pyrene, D_{12}-chrysene, D_{12}-benzo(a)pyrene, D_5-aniline, D_5-phenol, D_5-nitrobenzene, and D_3-2,4-dinitrophenol. The retention times and area counts obtained for each compound were monitored to assess the GC-MS performance.

6. Calibration samples containing 50 ng/µL of each of the 142 semivolatile compounds, which corresponds to a level of 25 µg/g in the Celite-clay, were analyzed daily to assess the GC-MS performance and to permit the percent recoveries of the compounds from Celite-clay to be calculated.

RESULTS AND DISCUSSION

The quantification limit for each compound was determined on the basis of the peak area response of the characteristic ion of the compound relative to the response of the characteristic ion of the D_{10}-phenanthrene added as an internal standard at the 50 ng/µL level, which represents 25 µg/g. The quantification limit was estimated as the concentration that gave a relative peak area of 0.01. Since the area count for the D_{10}-phenanthrene was usually at least 200,000, a relative peak area of 0.01 represents at least 2,000 counts. Responses of 2,000 area counts are usually reasonably reproducible for the GC-MS system used. Detection limits are usually lower by a factor of 5 to 10 relative to quantification limits estimated in the above manner; however, the quantitative responses at the lower levels are not sufficiently reproducible to provide reliable quantification.

The peak area ratios obtained at the four spike levels and the estimated quantification limits based on those data are given in Table 15. For 79 of the 142 compounds, the estimated quantification limit was 1 µg/g or less. For another 54 compounds the quantification limit was 2 to 5 µg/g. As expected, the quantification limits were frequently higher for the more polar compounds. However, even for most of the polar compounds such as phenols, anilines, and nitro compounds, the estimated quantification limits were 5 µg/g or lower. The only compounds spiked that could not be quantified at the 10 µg/g level were thiophenol, 4-bromobenzoic acid, 4-nitrophenol, 2,4-D, 2,4,5-T, and diethylstilbestrol.

The percent recoveries obtained for the compounds spiked into Celite and clay at the 25 µg/g level can be determined by comparing the peak area ratios obtained with those obtained from the analysis of the corresponding calibration solution. These data are given in Table 16. The recoveries obtained were 90 ± 20 percent for 129 of the 142 compounds.

TABLE 15. QUANTIFICATION LIMITS OF METHOD FOR DETERMINATION OF SEMIVOLATILE COMPOUNDS

No.	Compound	Peak Area Ratio[a] x 1000[b] at Given Concentration, µg/g					Estimated Quantification Limit[c], µg/g
		0	1	5	25	125	
1	4-Methylpyridine	<5	<5	60(7)	310(13)	1500(52)	2
2	1,4-Dichlorobutane	<5	20(19)	72(3)	340(15)	1900(7)	0.5
3	Anisole	<5	18(6)	81(4)	350(16)	NA[d]	1
4	Bromobenzene	<5	22(11)	85(7)	360(17)	1850(10)	0.5
5	2,4-Dimethylpridine	<5	5(72)	73(9)	370(19)	1340(40)	2
6	4-Chlorotoluene	<5	11(0)	43(0)	200(14)	1200(13)	1
7	2-Fluoraniline	<5	28(6)	110(1)	470(11)	NA	0.5
8	Benzaldehyde	<5	14(8)	60(4)	210(19)	NA	1
9	Thiophenol	21	11(62)	5(12)	12(10)	100(36)	50[e]
10	Pentachloroethane	<5	8(7)	33(2)	140(11)	840(10)	2
11	Aniline	<5	23(6)	110(13)	500(12)	2830(13)	0.5
12	Phenol	<5	<5	90(6)	280(37)	2370(12)	2
13	Bis(2-chloroethyl) ether	<5	22(16)	100(12)	380(11)	2300(10)	0.5
14	2-Chlorophenol	<5	20(3)	84(4)	360(12)	2040(12)	0.5
15	Pentafluorophenol	<5	<5	29(5)	120(6)	NA	4
16	1,2,4-Trimethylbenzene	<5	37(12)	150(3)	680(16)	3200(14)	0.3
17	2,4,6-Trimethylpyridine	<5	<5	57(14)	360(36)	1670(24)	2
18	1,4-Dichlorobenzene	<5	23(7)	110(10)	450(16)	2570(10)	0.5
19	Benzyl chloride	<5	34(3)	160(3)	670(13)	3230(14)	0.3
20	Benzyl alcohol	<5	12(44)	44(3)	220(5)	NA	1
21	1,2-Dichlorobenzene	<5	20(27)	110(10)	450(16)	1630(13)	0.5
22	2-Methylphenol	<5	14(15)	70(10)	320(24)	1950(11)	1
23	N-Methylaniline	<5	24(4)	110(4)	510(15)	2930(13)	0.5
24	Acetophenone	<5	28(16)	120(6)	560(15)	NA	0.5
25	4-Methylphenol	<5	10(97)	63(10)	300(8)	1950(11)	1
26	4-Methylaniline	<5	28(13)	120(22)	400(22)	1800(21)	0.5
27	Hexachloroethane	<5	9(18)	36(6)	150(12)	950(9)	2
28	Nitrobenzene	<5	10(12)	40(5)	180(12)	1180(13)	1
29	N,N-Dimethylaniline	<5	22(10)	100(9)	500(12)	2770(16)	0.5
30	4-t-Butylpyridine	<5	20(6)	100(4)	280(42)	1040(2)	0.5
31	1,2,4,5-Tetramethylbenzene	<5	34(8)	160(5)	700(17)	3380(15)	0.3
32	Decafluorobiphenyl	<5	4(16)	15(7)	73(13)	NA	5
33	4-Chlorobenzaldehyde	<5	10(26)	46(1)	160(29)	NA	1
34	2-Nitrophenol	<5	14(11)	40(11)	200(12)	1280(14)	1
35	Benzal chloride	<5	17(12)	84(5)	420(12)	2540(13)	1
36	2,4-Dimethylphenol	<5	10(15)	67(6)	300(14)	1960(12)	1
37	2-Nitrotoluene	<5	9(7)	46(9)	220(12)	1340(4)	2
38	Tetralin	<5	27(9)	120(7)	530(14)	2870(11)	0.5
39	Propiophenone	<5	42(7)	190(14)	950(9)	NA	0.3
40	2,6-Dimethylaniline	<5	20(15)	86(5)	390(10)	2120(8)	0.5
41	Benzoic acid	<5	<5	17(56)	51(121)	<5	5
42	2,6-Dichlorophenol	<5	6(91)	60(6)	270(14)	1720(16)	2

TABLE 15. (Continued)

No.	Compound	Peak Area Ratio[a] x 1000[b] at Given Concentration, µg/g					Estimated Quantification Limit[c], µg/g
		0	1	5	25	125	
43	1,2,4-Trichlorobenzene	<5	14(14)	62(8)	280(13)	1680(12)	1
44	Naphthalene	<5	49(10)	240(6)	970(15)	4220(10)	0.3
45	4-Chlorophenol	<5	<5	84(11)	440(8)	3200(18)	2
46	4-Chloroaniline	<5	5(53)	91(13)	450(13)	2430(12)	2
47	2,4-Dichlorophenol	<5	6(91)	59(6)	270(14)	1720(16)	2
48	Hexachloropropene	<5	<5	12(14)	42(38)	380(84)	5
49	4-Nitrotoluene	<5	8(7)	40(1)	190(12)	1200(14)	2
50	Hexachlorobutadiene	<5	6(18)	26(8)	120(11)	690(15)	2
51	Benzotrichloride	<5	7(8)	38(12)	210(20)	1600(13)	2
52	1-Chloro-4-nitrobenzene	<5	9(11)	36(7)	170(13)	1080(12)	2
53	Quinoline	<5	30(10)	170(5)	800(8)	4620(12)	0.4
54	Bis(2-chloroethoxy)ethane	<5	18(12)	87(10)	420(10)	2510(10)	1
55	4-Chloro-3-methylphenol	<5	12(12)	50(9)	950(14)	4100(13)	1
56	4-t-Butylphenol	<5	27(16)	140(8)	670(6)	3290(18)	0.5
57	4-Bromoaniline	<5	<5	43(8)	220(10)	1120(18)	2
58	2-Methylnaphthalene	<5	28(7)	140(8)	950(14)	NA	0.5
59	4-Chloro-2-methylaniline	<5	5(92)	61(3)	290(8)	1580(12)	2
60	4-Chlorobenzoic acid	<5	<5	<5	36(52)	200(62)	10
61	1,2,4,5-Tetrachlorobenzene	<5	10(22)	47(7)	220(11)	1320(14)	1
62	2,4,6-Trichlorophenol	<5	7(9)	35(11)	170(4)	1090(14)	2
63	2,4,5-Trichlorophenol	<5	7(17)	34(11)	170(4)	1000(13)	2
64	Acetanilide	<5	24(38)	160(10)	770(4)	NA	0.5
65	2-Chloronaphthalene	<5	33(25)	110(6)	1000(5)	2790(13)	0.4
66	Biphenyl	<5	37(7)	170(11)	760(8)	3330(11)	0.3
67	1-Chloronaphthalene	<5	33(25)	110(6)	1000(5)	2790(13)	0.4
68	5-Methylquinoline	<5	27(8)	150(8)	570(40)	NA	0.5
69	2-Ethylnaphthalene	<5	34(11)	160(7)	730(7)	4390(10)	0.3
70	Phenyl ether	<5	20(13)	92(8)	450(7)	NA	0.5
71	2-Nitroaniline	<5	9(16)	47(8)	250(5)	1480(9)	2
72	4-Bromobenzoic acid	<5	<5	<5	<5	150(21)	50
73	3,4-Dichloroaniline	<5	7(34)	67(8)	330(6)	2000(12)	2
74	2-Chloro-4-nitrophenol	<5	<5	9(51)	90(9)	630(10)	10
75	Acenaphthylene	<5	39(12)	150(9)	740(20)	2290(11)	0.3
76	2,3-Dimethylnaphthalene	<5	23(15)	110(2)	520(7)	2860(13)	0.5
77	1,3-Dinitrobenzene	<5	5(34)	30(2)	150(1)	970(8)	2
78	Dimethyl phthalate	<5	38(13)	190(5)	860(7)	NA	0.3
79	2,6-Dinitrotoluene	<5	7(14)	34(2)	190(6)	1210(8)	2
80	3-Nitroaniline	<5	<5	36(15)	220(7)	1220(7)	3
81	Acenaphthene	<5	27(9)	120(6)	580(8)	3130(11)	0.5
82	2,4-Di-t-butylphenol	<5	28(8)	140(3)	630(11)	3270(15)	0.5
83	2,4-Dinitrophenol	<5	<5	16(11)	84(6)	570(4)	5

TABLE 15. (Continued)

No.	Compound	Peak Area Ratio[a] x 1000[b] at Given Concentration, µg/g					Estimated Quantification Limit[c], µg/g
		0	1	5	25	125	
84	2-Naphthol	<5	<5	18(110)	130(89)	713(88)	5
85	2,6-Di-t-butyl-4-methylphenol	19	36(2)	82(26)	390(1)	1690(64)	1[e]
86	Dibenzofuran	<5	42(8)	200(4)	930(4)	NA	0.3
87	4-Nitrophenol	<5	<5	<5	5(113)	20(100)	100
88	Pentachlorobenzene	<5	8(12)	36(5)	170(8)	990(12)	2
89	2,4-Dinitrotoluene	<5	10(6)	48(2)	250(2)	1400(9)	1
90	1-Aminonaphthalene	<5	<5	36(30)	470(13)	3100(18)	3
91	2,4,5-Trichloroaniline	<5	10(16)	48(6)	250(10)	1290(12)	1
92	2,4-Dinitrochlorobenzene	<5	<5	15(8)	77(2)	460(4)	5
93	Fluorene	<5	30(6)	150(6)	710(4)	3440(11)	0.4
94	4-Chlorophenyl phenyl ether	<5	9(6)	45(8)	220(3)	1160(12)	2
95	4-Chloro-2-nitroaniline	<5	5(29)	33(8)	170(4)	930(6)	2
96	4-Nitroaniline	<5	<5	39(10)	210(7)	920(5)	3
97	2-Methyl-4,6-dinitrophenol	<5	<5	18(9)	110(4)	680(4)	5
98	Diphenylamine	<5	25(6)	130(3)	630(4)	3160(12)	0.5
99	Azobenzene	<5	8(8)	38(7)	180(3)	NA	2
100	Trifluoralin	<5	<5	14(4)	76(7)	560(9)	5
101	2-Chloro-4-nitroaniline	<5	<5	28(4)	140(1)	600(5)	3
102	4-Hydroxybiphenyl	<5	11(14)	120(11)	640(7)	3260(2)	1
103	Hexachlorobenzene	<5	5(11)	28(6)	140(7)	840(13)	2
104	2,6-Dichloro-4-nitroaniline	<5	<5	16(7)	81(1)	390(4)	5
105	2,4-Dichlorophenoxyacetic acid	<5	<5	<5	<5	<5	>100
106	4-Aminobiphenyl	<5	<5	60(8)	270(54)	2200(11)	3
107	Pentachlorophenol	<5	<5	6(44)	62(4)	410(2)	10
108	3,3'-Dichlorobiphenyl	<5	13(9)	65(10)	300(3)	NA	1
109	Pentachloronitrobenzene	<5	<5	10(6)	51(3)	100(10)	5
110	Phenanthrene	<5	45(12)	210(9)	1050(2)	4060(6)	0.3
111	4,4'-Dichlorobiphenyl	<5	13(9)	66(10)	330(5)	NA	1
112	Anthracene	<5	45(12)	210(9)	1050(2)	4060(6)	0.3
113	Acridine	<5	29(5)	130(6)	640(5)	2540(5)	0.5
114	Phenanthridine	<5	29(5)	140(11)	690(7)	2540(5)	0.5
115	Carbazole	<5	36(14)	200(5)	910(6)	3550(3)	0.3
116	2,4,5-Trichlorophenoxyacetic acid	<5	<5	<5	<5	<5	>100
117	Di-n-butyl phthalate	10	80(11)	390(5)	1840(9)	NA	0.2
118	2,4-Dinitroaniline	<5	<5	16(10)	63(15)	190(28)	5
119	2,2',4,4'-Tetrachlorobiphenyl	<5	5(11)	25(4)	120(2)	NA	2
120	Anthraquinone	<5	11(5)	53(2)	220(12)	NA	1
121	Fluoranthene	<5	40(3)	190(4)	800(11)	2620(11)	0.3
122	2,2',4,4',6,6'-Hexachlorobiphenyl	<5	5(11)	23(7)	120(6)	NA	2
123	2-Methylanthraquinone	<5	9(11)	42(6)	160(4)	NA	2
124	Pyrene	<5	41(1)	200(6)	800(7)	2310(14)	0.3
125	4,4'-DDE	<5	6(9)	31(5)	150(2)	590(15)	2

TABLE 15. (Continued)

No.	Compound	Peak Area Ratio[a] x 1000[b] at Given Concentration, µg/g					Estimated Quantification Limit[c], µg/g
		0	1	5	25	125	
126	4,4'-DDD	<5	9(16)	45(10)	190(1)	610(20)	2
127	Diethylstilbestrol	<5	<5	<5	<5	<5	>100
128	4,4'-DDT	<5	5(20)	23(5)	110(1)	390(20)	2
129	Triphenyl phosphate	<5	4(25)	17(3)	57(11)	NA	5
130	Benzo(a)anthracene	<5	30(10)	110(3)	350(12)	NA	0.4
131	Methoxychlor	<5	10(15)	53(4)	200(15)	440(32)	1
132	3,3'-Dichlorobenzidine	<5	5(29)	13(19)	7(20)	55(24)	2
133	Chrysene	<5	29(6)	110(3)	350(12)	NA	0.5
134	Bis(2-ethylhexyl) phthalate	8	88(74)	190(9)	700(9)	NA	0.2
135	Tri-(tolyl) phosphate	<5	<5	14(4)	90(23)	NA	5
136	Bis(2-ethylhexyl) sebacate	<5	17(16)	66(5)	240(12)	NA	1
137	Benzo(k)fluoranthene	<5	19(13)	75(3)	210(25)	NA	1
138	Benzo(a)pyrene	<5	22(12)	70(4)	180(22)	NA	0.5
139	Dibenzocarbazole	<5	12(10)	37(7)	85(10)	NA	1
140	Indeno(1,2,3-cd)pyrene	<5	12(26)	53(9)	130(19)	NA	1
141	Dibenzo(a,h)anthracene	<5	11(22)	45(3)	110(15)	NA	1
142	Benzo(g,h,i)perylene	<5	13(20)	52(9)	120(17)	NA	1

(a) Peak area ratio obtained for the compound spiked into Celite and clay at the given concentration divided by the peak area obtained for D_{10}-phenanthrene at a level of 50 µg/mL in the extract which represents 25 µg/g.

(b) The value given for the peak area ratio x 1000 is the average obtained from triplicate determinations except in the case of the control, 0 µg/g, for which only a single determination was made. The percent relative standard deviation is given in parentheses.

(c) The estimated quantification limit is the concentration level that would be expected to give an average peak area ratio of approximately 0.01, which represents a response equivalent to that obtained from 0.5 ng of D_{10}-phenanthrene injected onto the GC column.

(d) The compound was not added at this concentration level.

(e) The presence of this compound in the control sample was taken into account in the estimation of the quantification limit.

TABLE 16. RECOVERY OF SEMIVOLATILE ORGANIC COMPOUNDS FROM SPIKED CELITE AND CLAY

No.	Compound	Peak Area Ratio[a] x 1000[b] from Analysis of a Calibration Solution Containing 50 µg/mL	Peak Area Ratio[c] x 1000[b] from Analysis of Celite and Clay Spiked at a Level of 25 µg/g	Percent Recovery[d]
1	4-Methylpyridine	380 (8)	310 (13)	82
2	1,4-Dichlorobutane	380 (5)	340 (15)	89
3	Anisole	440 (7)	350 (16)	80
4	Bromobenzene	450 (6)	360 (17)	80
5	2,4-Dimethylpyridine	450 (6)	370 (19)	82
6	4-Chlorotoluene	240 (3)	200 (14)	83
7	2-Fluoroaniline	610 (2)	470 (11)	77
8	Benzaldehyde	240 (5)	210 (19)	88
9	Thiophenol	25 (6)	12 (10)	48
10	Pentachloroethane	180 (5)	140 (11)	78
11	Aniline	600 (5)	500 (12)	83
12	Phenol	260 (27)	280 (37)	108
13	Bis(2-chloroethyl) ether	460 (4)	380 (11)	83
14	2-Chlorophenol	460 (7)	360 (12)	78
15	Pentafluorophenol	160 (9)	120 (6)	75
16	1,2,4-Trimethylbenzene	870 (7)	680 (16)	78
17	2,4,6-Trimethylpyridine	500 (5)	360 (36)	72
18	1,4-Dichlorobenzene	570 (5)	450 (16)	79
19	Benzyl chloride	830 (8)	670 (13)	81
20	Benzyl alcohol	260 (7)	220 (5)	85
21	1,2-Dichlorobenzene	570 (5)	450 (16)	79
22	2-Methylphenol	380 (5)	320 (24)	84
23	N-Methylaniline	630 (6)	510 (15)	81
24	Acetophenone	660 (8)	560 (15)	85
25	4-Methylphenol	350 (4)	300 (8)	86
26	4-Methylaniline	510 (6)	400 (22)	78
27	Hexachloroethane	200 (8)	150 (12)	75
28	Nitrobenzene	220 (7)	180 (12)	82
29	N,N-Dimethylaniline	600 (5)	500 (12)	83
30	4-t-Butylpyridine	340 (31)	280 (42)	82
31	1,2,4,5-Tetramethylbenzene	860 (2)	700 (17)	81
32	Decafluorobiphenyl	86 (7)	73 (13)	85
33	4-Chlorobenzaldehyde	140 (2)	160 (29)	114
34	2-Nitrophenol	230 (6)	200 (12)	87
35	Benzal chloride	490 (6)	420 (12)	86
36	2,4-Dimethylphenol	370 (7)	300 (14)	81
37	2-Nitrotoluene	260 (6)	220 (12)	85
38	Tetralin	630 (4)	530 (14)	84
39	Propiophenone	1050 (5)	950 (9)	90
40	2,6-Dimethylaniline	450 (6)	390 (10)	87
41	Benzoic acid	95 (86)	51 (121)	54

TABLE 16. (Continued)

No.	Compound	Peak Area Ratio[a] x 1000[b] from Analysis of a Calibration Solution Containing 50 µg/mL	Peak Area Ratio[c] x 1000[b] from Analysis of Celite and Clay Spiked at a Level of 25 µg/g	Percent Recovery[d]
42	2,6-Dichlorophenol	310 (5)	270 (14)	87
43	1,2,4-Trichlorobenzene	320 (5)	280 (13)	88
44	Naphthalene	1180 (4)	970 (15)	82
45	4-Chlorophenol	510 (5)	440 (8)	86
46	4-Chloroaniline	500 (4)	450 (13)	90
47	2,4-Dichlorophenol	310 (5)	270 (14)	87
48	Hexachloropropene	90 (3)	42 (38)	47
49	4-Nitrotoluene	210 (4)	190 (12)	90
50	Hexachlorobutadiene	130 (2)	120 (11)	92
51	Benzotrichloride	250 (9)	210 (20)	84
52	1-Chloro-4-nitrobenzene	190 (8)	170 (13)	89
53	Quinoline	890 (7)	800 (8)	90
54	Bis(2-chloroethoxy)ethane	460 (3)	420 (10)	91
55	4-Chloro-3-methylphenol	1030 (5)	950 (14)	92
56	4-t-Butylphenol	720 (5)	670 (6)	93
57	4-Bromoaniline	240 (6)	220 (10)	92
58	2-Methylnaphthalene	1040 (5)	950 (14)	91
59	4-Chloro-2-methylaniline	320 (5)	290 (8)	91
60	4-Chlorobenzoic acid	89 (6)	36 (52)	40
61	1,2,4,5-Tetrachlorobenzene	260 (2)	220 (11)	85
62	2,4,6-Trichlorophenol	190 (5)	170 (4)	89
63	2,4,5-Trichlorophenol	190 (3)	170 (4)	89
64	Acetanilide	830 (7)	770 (4)	93
65	2-Chloronaphthalene	1140 (5)	1000 (5)	88
66	Biphenyl	850 (11)	760 (8)	89
67	1-Chloronaphthalene	1090 (21)	1000 (5)	92
68	5-Methylquinoline	700 (7)	570 (40)	81
69	2-Ethylnaphthalene	850 (3)	730 (7)	73
70	Phenyl ether	480 (4)	450 (7)	94
71	2-Nitroaniline	280 (5)	250 (5)	89
72	4-Bromobenzoic acid	26 (14)	ND (e)	(f)
73	3,4-Dichloroaniline	360 (4)	330 (6)	92
74	2-Chloro-4-nitrophenol	100 (2)	90 (9)	90
75	Acenaphthylene	470 (5)	650 (7)	138
76	2,3-Dimethylnaphthalene	580 (4)	520 (7)	90
77	1,3-Dinitrobenzene	170 (5)	150 (1)	88
78	Dimethyl phthalate	930 (5)	860 (7)	92
79	2,6-Dinitrotoluene	200 (1)	190 (6)	95
80	3-Nitroaniline	230 (2)	220 (7)	96
81	Acenaphthene	630 (5)	580 (8)	92
82	2,4-Di-t-butylphenol	710 (6)	630 (11)	89

TABLE 16. (Continued)

No.	Compound	Peak Area Ratio[a] x 1000[b] from Analysis of a Calibration Solution Containing 50 µg/mL	Peak Area Ratio[c] x 1000[b] from Analysis of Celite and Clay Spiked at a Level of 25 µg/g	Percent Recovery[d]
83	2,4-Dinitrophenol	97 (6)	84 (6)	87
84	2-Naphthol	180 (11)	130 (89)	72
85	2,6-Di-t-butyl-4-methylphenol	380 (11)	390 (1)	103
86	Dibenzofuran	1000 (3)	930 (4)	93
87	4-Nitrophenol	4 (71)	5 (113)	120
88	Pentachlorobenzene	190 (4)	170 (8)	89
89	2,4-Dinitrotoluene	260 (3)	250 (2)	96
90	1-Aminonaphthalene	460 (6)	470 (13)	102
91	2,4,5-Trichloroaniline	270 (4)	250 (10)	93
92	2,4-Dinitrochlorobenzene	80 (2)	77 (2)	96
93	Fluorene	740 (7)	710 (4)	96
94	4-Chlorophenyl phenyl ether	230 (4)	220 (3)	96
95	4-Chloro-2-nitroaniline	180 (6)	170 (4)	94
96	4-Nitroaniline	220 (9)	210 (7)	95
97	2-Methyl-4,6-dinitrophenol	110 (6)	110 (4)	100
98	Diphenylamine	650 (6)	630 (4)	97
99	Azobenzene	200 (2)	180 (3)	90
100	Trifluralin	80 (7)	76 (7)	96
101	2-Chloro-4-nitroaniline	150 (8)	140 (1)	93
102	4-Hydroxybiphenyl	700 (3)	640 (7)	91
103	Hexachlorobenzene	150 (3)	140 (7)	93
104	2,6-Dichloro-4-nitroaniline	83 (2)	81 (1)	98
105	2,4-Dichlorophenoxyacetic acid	ND (e)	ND	(f)
106	4-Aminobiphenyl	230 (50)	270 (54)	117
107	Pentachlorophenol	67 (4)	62 (4)	93
108	3,3'-Dichlorobiphenyl	310 (6)	300 (3)	97
109	Pentachloronitrobenzene	54 (4)	51 (3)	94
110	Phenanthrene	1070 (4)	1050 (2)	98
111	4,4'-Dichlorobiphenyl	340 (4)	330 (5)	97
112	Anthracene	1080 (4)	1050 (2)	97
113	Acridine	710 (5)	640 (5)	90
114	Phenanthridine	750 (5)	690 (7)	92
115	Carbazole	980 (10)	910 (6)	93
116	2,4,5-Trichlorophenoxyacetic acid	ND	ND	(f)
117	Di-n-butyl phthalate	1910 (8)	1840 (9)	96
118	2,4-Dinitroaniline	84 (26)	63 (15)	75
119	2,2',4,4'-Tetrachlorobiphenyl	120 (7)	120 (2)	100
120	Anthraquinone	230 (12)	220 (12)	96
121	Fluoranthene	860 (14)	800 (11)	93
122	2,2',4'4,6,6'-Hexachlorobiphenyl	120 (7)	120 (6)	100
123	2-Methylanthraquinone	160 (20)	160 (4)	100

TABLE 16. (Continued)

No.	Compound	Peak Area Ratio[a] x 1000[b] from Analysis of a Calibration Solution Containing 50 µg/mL	Peak Area Ratio[c] x 1000[b] from Analysis of Celite and Clay Spiked at a Level of 25 µg/g	Percent Recovery[d]
124	Pyrene	830 (14)	800 (7)	96
125	4,4'-DDE	150 (7)	150 (2)	100
126	4,4'-DDD	190 (16)	190 (1)	100
127	Diethylstilbestrol	6 (55)	ND	(f)
128	4,4'-DDT	110 (24)	110 (1)	100
129	Triphenyl phosphate	57 (22)	57 (11)	100
130	Benzo(a)anthracene	360 (19)	350 (12)	97
131	Methoxychlor	220 (33)	200 (15)	91
132	3,3'-Dichlorobenzidine	17 (120)	7 (20)	41
133	Chrysene	360 (19)	350 (12)	97
134	Bis(2-ethylhexyl) phthalate	720 (22)	700 (9)	97
135	Tri-(tolyl) phosphate	40 (21)	40 (23)	100
136	Bis(2-ethylhexyl) sebacate	250 (26)	240 (12)	96
137	Benzo(k)fluoranthene	210 (23)	210 (25)	100
138	Benzo(a)pyrene	180 (26)	180 (22)	100
139	Dibenzocarbazole	110 (23)	85 (10)	77
140	Indeno(1,2,3-cd)pyrene	120 (35)	130 (19)	108
141	Dibenzo(a,h)anthracene	120 (22)	110 (15)	92
142	Benzo(g,h,i)perylene	120 (40)	120 (17)	100

(a) Peak area obtained for the compound spiked into methylene chloride at a level of 50 µg/mL divided by the peak area obtained for D_{10}-phenanthrene at a level of 50 µg/mL.

(b) The value given for the peak area ratio x 1000 is the average obtained from triplicate determinations. The percent relative standard deviation is given in parentheses.

(c) Peak area obtained from the compound spiked into Celite and clay at a level of 25 µg/g divided by the peak area obtained for D_{10}-phenanthrene added to the extract at a level of 50 µg/mL which represents 25 µg/g.

(d) Percent Recovery = $\frac{\text{Peak Area Ratio from Analysis of Spiked Celite and Clay}}{\text{Peak Area Ratio from Analysis of Calibration Solution}} \times 100$

(e) Not detected.

(f) Not determined because the compound was not detected at this concentration level.

TASK 3. COMPARISON OF SOLVENTS FOR THE EXTRACTION OF SEMIVOLATILE COMPOUNDS

INTRODUCTION

Methylene chloride was used in the dry neutral sonification extraction procedure for extracting solid wastes because it is known to be a good solvent for a wide variety of organic compounds and is the solvent of choice for wastewater extraction. Methylene chloride extracts can be readily analyzed using GC-MS. In the interest of lowering analytical costs, the analysis of solid waste extracts using less expensive instrumentation was considered. Two approaches of interest were the determination of nitrogen-containing compounds by GC analysis using a nitrogen-specific thermionic detector and the determination of the TOX using a microcoulimetric technique. Unfortunately, methylene chloride and other chlorinated solvents are not acceptable for use in either of these two approaches. Therefore, methyl tert-butyl ether, a nonchlorinated solvent with a polarity somewhat similar to that of methylene chloride, was proposed as an alternate solvent. Methyl tert-butyl ether was chosen instead of diethyl ether because, unlike diethyl ether, it does not form peroxides. Task 3 was undertaken to compare the extraction efficiency of methyl tert-butyl ether with that of methylene chloride for the extraction of semivolatile components from a variety of solid wastes.

EXPERIMENTAL

Three aliquots of each of six spiked waste samples prepared previously for an interlaboratory study (8) were extracted with methylene chloride using the dry neutral sonification procedure (6). Another three aliquots of each of the six samples were extracted similarly using methyl tert-butyl ether instead of methylene chloride. Residue weights were obtained for the filtered extracts by evaporating a 100-µL aliquot of the extract on a small aluminum disc under controlled conditions and weighing the residue on a Mettler ME-30 microbalance. The extracts were analyzed by GC-FID using a Hewlett Packard Model 5730 gas chromatograph fitted with a 30 m x 0.25 mm I.D. SE-52 glass capillary column. Those components that were adequately resolved were quantified using an external sandard approach.

RESULTS AND DISCUSSION

The residue weights obtained for the filtered extracts are given in Table 17. The amounts of the individual semivolatile compounds that could be quantified by GC-FID are given in Tables 18 to 23. The ratio of the amounts found in methyl tert-butyl ether extracts to the amounts in the methylene chloride extracts, included in the tables, show very clearly that methyl tert-butyl ether is not as effective as methylene chloride under the conditions used. The lower extraction efficiency appears to be associated with the lower density of methyl tert-butyl ether, which prevents the sodium sulfate, and material adsorbed on the sodium sulfate, from being suspended and acted upon by sonic energy during the

TABLE 17. RESIDUE WEIGHTS OF MTBE AND CH_2Cl_2 EXTRACTS OF WASTES

Sample	Residue Wt. Using MTBE, mg/g of Sample	Residue Wt. Using CH_2Cl_2, mg/g of Sample	Res. Wt. Using MTBE / Res. Wt. Using CH_2Cl_2
1. Spiked contaminated soil (ILS-1)[a]	37	46	0.80
2. Spiked latex paint (ILS-2)	15	57	0.26
3. Spiked ethanes spent catalyst (ILS-3)	130	220	0.59
4. Spiked coal gasification tar (ILS-4)	230	600	0.38
5. Spiked oxychlorination spent catalyst (ILS-5)	0.4	0.7	0.57
6. Spiked chemically treated POTW sludge (ILS-6)	10	17	0.59

(a) The ILS numbers were used to identify the spiked wastes analyzed in the interlaboratory study (8).

TABLE 18. SEMIVOLATILE COMPOUNDS EXTRACTED FROM SPIKED CONTAMINATED SOIL (ILS-1) USING MTBE AND CH_2Cl_2

Compound	Amt. Found Using MTBE µg/g(a)	% RSD	Amt. Found Using CH_2Cl_2 µg/g(a)	% RSD	Amt. Found Using MTBE / Amt. Found Using CH_2Cl_2
4-t-Butylpyridine	180	4	180	22	1.0
2,4-Dimethylphenol	210	7	220	27	0.96
Propiophenone	300	3	340	22	0.88
4-Chloroaniline	(b)	(b)	(b)	(b)	(b)
Quinoline	46	3	50	22	0.92
Bis(2-chloroethoxy)ethane	300	2	300	19	1.0
4-Chloro-2-methylaniline	52	21	88	41	0.59
Biphenyl	68	2	130	20	0.52
4-Methylquinoline	49	6	64	19	0.77
1,3-Dinitrobenzene	200	5	250	14	0.80
Acenaphthene	110	11	140	15	0.79
Pentachlorobenzene	210	7	260	18	0.82
Fluorene	17	10	21	17	0.81
Hexachlorobenzene	(b)	(b)	(b)	(b)	(b)
Anthracene	53	6	64	17	0.82
Anthraquinone	42	9	46	26	0.91
Fluoranthene	710	5	800	13	0.89
Pyrene	840	5	920	17	0.91
DDD	120	8	110	21	1.1
DDT	180	17	190	21	0.95
Triphenyl phosphate	84	5	70	11	1.2
Tri-p-tolyl phosphate	180	6	180	26	1.0

(a) Average values obtained from three extractions.

(b) Not applicable because the compound was not detected; the compound had been spiked into the sample at a relatively low level.

TABLE 19. SEMIVOLATILE COMPOUNDS EXTRACTED FROM SPIKED LATEX PAINT WASTE (ILS-2) USING MTBE AND CH_2Cl_2

Compound	Amt. Found Using MTBE µg/g(a)	% RSD	Amt. Found Using CH_2Cl_2 µg/g(a)	% RSD	Amt. Found Using MTBE / Amt. Found Using CH_2Cl_2
4-t-Butylpyridine	3100	7	4400	5	0.70
2,4-Dimethylphenol	220	6	300	6	0.72
Propiophenone	710	5	960	7	0.74
4-Chloroaniline	490	5	620	9	0.79
Quinoline	840	6	950	9	0.88
Bis(2-chloroethoxy)ethane	(b)	(b)	(b)	(b)	(b)
4-Chloro-2-methylaniline	110	5	130	17	0.87
Biphenyl	69	7	100	12	0.69
4-Methylquinoline	670	2	910	9	0.74
1,3-Dinitrobenzene	560	6	670	7	0.84
Acenaphthene	(b)	(b)	(b)	(b)	(b)
Pentachlorobenzene	(b)	(b)	(b)	(b)	(b)
Fluorene	(b)	(b)	(b)	(b)	(b)
Hexachlorobenzene	850	2	1200	5	0.71
Anthracene	(b)	(b)	(b)	(b)	(b)
Anthraquinone	780	8	1100	8	0.71
Fluoranthene	130	4	170	10	0.78
Pyrene	530	5	690	8	0.77
DDD	180	9	200	0	0.88
DDT	430	7	580	16	0.74
Triphenyl phosphate	790	9	920	6	0.86
Tri-p-tolyl phosphate	150	10	170	10	0.86

(a) Average values obtained from three extractions.

(b) Not applicable because the compound was not detected; the compound was spiked into the sample at a relatively low level.

TABLE 20. SEMIVOLATILE COMPOUNDS EXTRACTED FROM SPIKED ETHANES SPENT CATALYST (ILS-3) USING MTBE AND CH_2Cl_2

Compound	Amt. Found Using MTBE µg/g(a)	% RSD	Amt. Found Using CH_2Cl_2 µg/g(a)	% RSD	Amt. Found Using MTBE / Amt. Found Using CH_2Cl_2
4-t-Butylpyridine	(b)	(b)	(b)	(b)	(b)
2,4-Dimethylphenol	(b)	(b)	(b)	(b)	(b)
Propiophenone	220	5	260	11	0.85
4-Chloroaniline	2200	5	3200	5	0.69
Quinoline	230	5	2300	3	0.10
Bis(2-chloroethoxy)ethane	3000	5	3200	9	0.94
4-Chloro-2-methylaniline	(b)	(b)	(b)	(b)	(b)
Biphenyl	480	18	450	19	1.1
4-Methylquinoline	420	2	560	2	0.75
1,3-Dinitrobenzene	410	1	510	13	0.80
Acenaphthene	760	4	860	1	0.88
Pentachlorobenzene	(b)	(b)	(b)	(b)	(b)
Fluorene	1900	3	2200	3	0.86
Hexachlorobenzene	1700	6	1900	3	0.89
Anthracene	(b)	(b)	(b)	(b)	(b)
Anthraquinone	5300	2	5300	3	1.0
Fluoranthene	2100	3	2500	0	0.84
Pyrene	(b)	(b)	(b)	(b)	(b)
DDD	1600	26	1700	3	0.95
DDT	(b)	(b)	(b)	(b)	(b)
Triphenyl phosphate	1500	0	1400	8	1.1
Tri-p-tolyl phosphate	390	3	350	6	1.1

(a) Average values obtained from three extractions.

(b) Not applicable because the compound was not detected; the compound had been spiked into the sample at a relatively low level.

TABLE 21. SEMIVOLATILE COMPOUNDS EXTRACTED FROM SPIKED COAL GASIFICATION TAR (ILS-4) USING MTBE AND CH_2Cl_2

Compound	Amt. Found Using MTBE µg/g(a)	% RSD	Amt. Found Using CH_2Cl_2 µg/g(a)	% RSD	Amt. Found Using MTBE / Amt. Found Using CH_2Cl_2
4-t-Butylpyridine	4600	35	5700	10	0.81
2,4-Dimethylphenol	10,000	34	7600	6	1.3
Propiophenone	9300	33	9100	6	1.0
4-Chloroaniline	1900	34	1170	5	1.6
Quinoline	2600	38	1900	8	1.4
Bis(2-chloroethoxy)ethane	(b)	(b)	(b)	(b)	(b)
4-Chloro-2-methylaniline	10,000	33	13,000	15	0.77
Biphenyl	2000	31	1400	9	1.4
4-Methylquinoline	1500	33	1200	8	1.3
1,3-Dinitrobenzene	35,000	34	33,000	9	1.1
Acenaphthene	(b)	(b)	(b)	(b)	(b)
Pentachlorobenzene	10,000	33	7800	8	1.3
Fluorene	11,000	35	8500	8	1.3
Hexachlorobenzene	2300	33	2000	8	1.2
Anthracene	9800	34	8200	6	1.2
Anthraquinone	2400	31	2100	7	1.1
Fluoranthene	17,000	31	14,000	7	1.2
Pyrene	21,000	31	18,000	6	1.2
DDD	3200	30	2500	8	1.3
DDT	10,200	42	8400	28	1.2
Triphenyl phosphate	3400	26	2700	6	1.3
Tri-p-tolyl phosphate	9100	35	7900	8	1.2

(a) Average value obtained from three extractions.

(b) Not applicable because the compound was not detected; the compound had been spiked into the sample at a relatively low level.

TABLE 22. SEMIVOLATILE COMPOUNDS EXTRACTED FROM SPIKED SPENT OXYCHLORINATION CATALYST (ILS-5) USING MTBE AND CH_2Cl_2

Compound	Amt. Found Using MTBE µg/g(a)	% RSD	Amt. Found Using CH_2Cl_2 µg/g(a)	% RSD	Amt. Found Using MTBE / Amt. Found Using CH_2Cl_2
4-t-Butylpyridine	8.2	6	8.3	41	0.99
2,4-Dimethylphenol	(b)	(b)	(b)	(b)	(b)
Propiophenone	21	18	21	22	1.0
4-Chloroaniline	(b)	(b)	(b)	(b)	(b)
Quinoline	21	3	26	21	0.81
Bis(2-chloroethoxy)ethane	11	19	10	22	1.1
4-Chloro-2-methylaniline	(b)	(b)	(b)	(b)	(b)
Biphenyl	2.6	20	2.7	10	0.96
4-Methylquinoline	31	12	33	13	0.93
1,3-Dinitrobenzene	16	45	35	11	0.46
Acenaphthene	(b)	(b)	(b)	(b)	(b)
Pentachlorobenzene	28	20	30	25	0.93
Fluorene	1.1	14	1.0	15	1.1
Hexachlorobenzene	18	51	11	23	1.6
Anthracene	5.2	60	8.0	15	0.65
Anthraquinone	3.4	32	5.0	24	0.68
Fluoranthene	3.7	39	5.3	30	0.70
Pyrene	15	21	20	18	0.75
DDD	9.6	39	8.9	31	1.1
DDT	38	29	31	16	1.2
Triphenyl phosphate	9.7	39	8.3	18	1.2
Tri-p-tolyl phosphate	26	45	29	26	0.90

(a) Average values obtained from three extractions.

(b) Not applicable because the compound was not detected; the compound had been spiked into the sample at a relatively low level.

TABLE 23. SEMIVOLATILE COMPOUNDS EXTRACTED FROM SPIKED CHEMICALLY-TREATED POTW SLUDGE (ILS-6) USING MTBE AND CH_2Cl_2

Compound	Amt. Found Using MTBE µg/g(a)	% RSD	Amt. Found Using CH_2Cl_2 µg/g(a)	% RSD	Amt. Found Using MTBE / Amt. Found Using CH_2Cl_2
4-t-Butylpyridine	54	36	200	9	0.27
2,4-Dimethylphenol	78	12	190	8	0.41
Propiophenone	30	22	130	24	0.23
4-Chloroaniline	(b)	(b)	(b)	(b)	(b)
Quinoline	(b)	(b)	(b)	(b)	(b)
Bis(2-chloroethoxy)ethane	63	13	160	5	0.39
4-Chloro-2-methylaniline	58	16	130	8	0.45
Biphenyl	20	36	76	3	0.26
4-Methylquinoline	29	30	130	0	0.22
1,3-Dinitrobenzene	26	33	120	5	0.21
Acenaphthene	29	29	120	0	0.24
Pentachlorobenzene	42	31	170	3	0.25
Fluorene	26	27	100	0	0.26
Hexachlorobenzene	(b)	(b)	(b)	(b)	(b)
Anthracene	(b)	(b)	(b)	(b)	(b)
Anthraquinone	13	16	31	0	0.42
Fluoranthene	7.5	32	33	15	0.23
Pyrene	170	15	340	10	0.50
DDD	19	28	60	3	0.32
DDT	(b)	(b)	(b)	(b)	(b)
Triphenyl phosphate	19	11	24	15	0.79
Tri-p-tolyl phosphate	61	42	230	4	0.27

(a) Average values obtained from three extractions.

(b) Not applicable because the compound was not detected; the compound had been spiked into the sample at a relatively low level.

sonification step. Very dramatic differences in the degree to which solid was suspended in the two solvents were observed during the sonification step. The effect is particularly apparent in the results obtained from the extraction of spiked POTW sludge, ILS-6, (see Table 23) compared with those from the extraction of spiked coal tar, ILS-4 (see Table 21). In the case of the coal tar, the sample is very lipophilic and disperses readily in either solvent prior to the addition of sodium sulfate. Hence methyl tert-butyl ether is as effective as methylene chloride for the extraction of coal tar. However, in the case of POTW sludge, the sample is very wet and lipophobic and does not disperse well in either solvent. Therefore, much of the extraction probably takes place after the sodium sulfate is added. Since the sodium sulfate and other solid material are not well dispersed in methyl tert-butyl ether during the sonification step, the recoveries are much lower than those obtained from the use of methylene chloride.

TASK 4. STUDY OF MATRIX EFFECTS ON DETERMINATION OF PURGEABLE COMPOUNDS

INTRODUCTION

The determination of purgeable compounds in solid wastes by the tetraglyme extraction method involves the addition of an aliquot of a tetraglyme extract to water and purging the mixture to transfer the purgeable components to an analytical system. The tetraglyme extract contains all of the extractable nonpurgeable components present in the sample as well as the purgeable components. Task 4 was undertaken to determine whether the extractable nonpurgeable components of a waste may sometimes interfere with the purging efficiency of the purgeable components.

EXPERIMENTAL

Tetraglyme extracts of unspiked aliquots of the nine wastes listed in Table 1 for Task 1 and a tetraglyme blank were analyzed with and without spiking with 12 representative purgeable compounds using GC-PID/Hall analysis and using the Dohrmann microcoulimetric POX analysis procedure.

Extraction of Wastes

A 2.0-gram aliquot of unspiked waste was added to 40 mL of tetraglyme in a 50-mL screw-cap vial with a Teflon-lined septum. The vial was shaken vigorously for one minute and allowed to stand at least overnight in a refrigerator to permit phase separation. A clear supernatant was obtained in each case. The vial was protected from contamination in the refrigerator by sealing the vial in a one-quart paint can placed inside a sealed one-gallon paint can containing activated charcoal.

Spiking of Extracts

Ten-milliliter aliquots of the tetraglyme extracts were spiked with a methanol solution containing 1 µg/µL of each of the 12 representative volatile compounds listed in Table 24. All extracts except that from the ethanes spent catalyst were spiked at a level representing 40 µg of each analyte per gram of sample, 2 µg/mL of extract. Since the background POX level was considerably higher in the extract from the ethanes spent catalyst, this extract was spiked at a level representing 2000 µg of each analyte per gram of sample, 100 µg/mL of extract. The extracts from six samples, namely contaminated soil, latex paint waste, oxychlorination spent catalyst, oil refining waste, Zimpro POTW sludge, and wet POTW sludge, had very low background POX levels and were spiked at a level representing 10 µg of each analyte per gram of sample as well as the 40 µg/g level.

TABLE 24. COMPOUNDS SPIKED INTO TETRAGLYME EXTRACTS OF WASTES

Allyl chloride	Benzene
Bromoethane	1,1,1-Trichloroethane
Bromoform	2-Hexanone
Chlorobenzene	1,1,2,2-Tetrachloroethane
1,2-Dichloroethane	Ethylbenzene
1,2-Dichloropropane	o-Xylene

GC-PID/Hall Analysis

A 200-µL aliquot of the spiked or unspiked tetraglyme extract was added to 4.8 mL of distilled water in a 5-mL purging tube and spiked with 10 µL of a methanol solution containing 100 ng/µL of 4-bromofluorobenzene (BFB) as an internal standard. The sample was analyzed by GC-PID/Hall analysis in accordance with EPA Methods 601 and 602. A Tracor Model 560 gas chromatograph fitted with an HNU photoionization detector, equipped with a 10.2 e.v. lamp, in series with a Tracor Model 700A Hall electrolytic conductivity detector, operated in the halogen mode, was used for the GC analysis. A Tekmar Model ALS automatic sampler interfaced with a Tekmar Model LSC-2 automatic purge and trap concentrator was used for the purge and trap steps.

POX Analysis

A Dohrmann MC-1/DX-20 Total Organic Halide Analyzer System was used for the POX analyses. The system is comprised of a thermostated sample purging tube, a heated pyrolysis tube, and a microcoulimetric halide titration cell. Aqueous samples are added to the purging tube through a syringe valve. The volatile organic halogen compounds are purged from a sample by a stream of CO_2, swept into the pyrolysis chamber, and pyrolyzed to form HX. The HX is swept into the microcoulometric titration cell and quantified by an automated titration with silver ions. The instrument gives a direct reading of the total molar quantity of halogens expressed as micrograms of chloride.

A measured volume of tetraglyme extract was added by syringe to a 10-mL syringe containing 7 mL of organic-free water and one drop of 10 percent Antifoam B emulsion to retard foaming. The volume of tetraglyme extract used was 1 mL for all samples except the ethanes spent catalyst, in which case 20 µL of extract was used. The instrument analysis cycle was started and the sample in the 10-mL syringe was added to the purging tube through a syringe valve. After 10 minutes of purging, the total chloride value given by the instrument was recorded, the sample was removed from the purging tube, and the purging tube was rinsed with organic-free water to prepare for the next analysis. All samples, standards, and blanks were analyzed in triplicate.

RESULTS AND DISCUSSION

The results from the GC-PID/Hall analyses were too variable to permit any matrix effects to be detected. The variability is indicated by the response factors obtained from the periodic analysis of a calibration solution during the period that the sample extracts were analyzed. The calibration solution contained 20 ng/μL of each of the 12 compounds in Table 24; 10 μL of the solution was added to the purging tube. The response factors obtained from 12 calibration runs are given in Table 25. In most cases the relative standard deviations of the response factors were greater than 40 percent, and the low and high values for the response factors of any one compound differed by a factor of 3 to 10. The variability was probably caused by contamination of the transfer lines and GC column by small amounts of entrained tetraglyme, antifoam and other high-boiling components. The presence of high-boiling interfering components was very apparent from the GC-PID chromatograms. The components apparently did not contain halogen since they did not show up on the GC-Hall chromatograms; nevertheless, the presence of variable amounts of such components in the GC column could have affected the GC-Hall quantification. The presence of such components in the transfer lines would absorb the purgeable components of interest and give highly variable results. Variabilities caused by high-boiling components were avoided in the GC-MS studies described in Task 2 by sweeping the transfer line and GC column with carrier gas for an additional 30 minutes at the end of each run and by controlling the purge gas flow to ensure that no entrained liquid entered the transfer line.

The results obtained from the POX analyses are given in Table 26. In most cases the relative percent recoveries were 100 ± 5 percent indicating that the total extractable matrix generally has no effect on the results of POX determinations. The most significant indication of a matrix effect was found with the Zimpro POTW sludge extract spiked at the low level, in which case the relative recovery was only 74 percent. However, it should be noted that in this case the spike level was only two times the background level in the unspiked sample. At a higher spike level there was no matrix effect. In two other cases, the ethanes catalyst extract and the wet POTW sludge extract spiked at the low level, the relative recoveries were 89 and 90 percent, respectively, which may indicate a slight matrix effect. We conclude from the results that there are no significant matrix effects.

QUALITY ASSURANCE

The precision or repeatability of the POX determinations is documented by the data presented in Table 27. The relative standard deviations were very low. In 20 of the 21 cases in which the total POX in

TABLE 25. RESPONSE FACTORS OF PURGEABLE COMPOUNDS OBTAINED FROM CALIBRATION RUNS USING GC-PID/HALL ANALYSIS

Run No.	Response Factor[a] Obtained for Given Compound Using Hall Detector								Response Factor[a] Obtained for Given Compound Using PID				
	Bromo-ethane	Allyl Chloride	1,2-Dichloro-ethane	1,1,1-Tri-chloroethane	1,2-Dichloro-propane	Bromo-form	1,1,2,2-Tetra-chloroethane	Chloro-benzene	Chloro-benzene	Benzene	2-Hexanone	Ethyl-benzene	o-Xylene
229	0.54	0.92	0.73	3.60	2.21	1.17	1.42	0.04	0.20	(b)	(b)	0.45	1.16
232	0.47	0.70	0.51	3.55	1.95	1.18	1.37	0.05	(b)	(b)	(b)	(b)	(b)
236	0.21	0.50	0.16	1.62	0.73	0.51	0.89	0.10	(b)	(b)	(b)	(b)	0.96
242	0.28	0.34	0.19	2.14	0.77	0.82	0.65	0.04	(b)	(b)	(b)	(b)	0.63
248	0.31	0.49	0.22	2.06	1.02	0.59	1.00	0.09	(b)	(b)	(b)	(b)	(b)
251	0.24	0.54	0.26	1.42	0.85	0.43	0.92	0.22	0.27	(b)	0.15	0.38	0.76
279	0.25	0.31	0.83	0.83	0.66	0.24	0.74	0.35	0.15	(b)	0.38	0.93	0.93
289	0.20	0.17	0.48	1.03	0.71	0.33	0.75	0.31	0.24	(b)	0.31	0.54	0.67
298	0.33	0.46	1.08	1.20	1.01	0.46	1.09	0.48	(b)	(b)	(b)	(b)	0.67
301	0.22	0.28	0.77	0.74	0.65	0.33	0.73	0.33	(b)	(b)	(b)	(b)	(b)
303	0.22	0.25	0.76	0.78	0.66	0.28	0.72	0.34	(b)	(b)	(b)	(b)	(b)
308	0.19	0.23	0.64	0.80	0.69	0.27	0.73	0.30	(b)	(b)	(b)	(b)	(b)
Avg.	0.29	0.43	0.55	1.65	0.99	0.55	0.92	0.22	0.22	--	0.28	0.58	0.83
% RSD	39	51	55	62	54	61	28	68	24	--	42	43	24

(a) Response Factor = $\frac{\text{Area of compound}}{\text{Area of BFB}} \times \frac{\text{ng of BFB}}{\text{ng of compound}}$

(b) Not quantifiable because of interference from high-boiling compounds.

TABLE 26. RECOVERY OF POX SPIKED INTO TETRAGLYME EXTRACTS OF WASTES

Waste Sample	Amount of POX Spiked: µg of Each Component per g of Waste	Amount of POX Spiked: Total POX as µg of Cl per mL of Extract[a]	Amount of POX Found as µg of Cl per mL of Extract[a]: Unspiked	Amount of POX Found as µg of Cl per mL of Extract[a]: Spiked	Percent Recovery[b]	Relative Percent Recovery[c]
Contaminated Soil	10	2.22	0.35	2.07	77	101
	40	8.88		7.94	85	105
Latex Paint Waste	10	2.22	0.19	1.84	74	97
	40	8.88		7.89	87	107
Ethanes Catalyst	2000	8.12[d]	2.31[d]	8.47[d]	76	89
Coal Gasif. Tar	40	8.88	2.99	10.50	85	104
Oxychlor. Catalyst	10	2.22	0.39	2.07	76	99
	40	8.88		7.75	83	102
Treated POTW Sludge	40	8.88	2.30	9.24	78	96
Oil Refining Waste	10	2.22	0.35	2.01	75	98
	40	8.88		7.95	86	105
Zimpro POTW Sludge	10	2.22	1.24	2.49	56	74
	40	8.88		8.26	79	97
Wet POTW Sludge	10	2.22	0.17	1.70	69	90
	40	8.88		7.15	79	97
Tetraglyme Blank	--	2.22	0.08	1.70	73	100
	--	8.88		7.22	80	100

(a) Average of triplicate determinations

(b) $$\text{Percent Recovery} = \frac{\text{Amount Found in Spiked Sample} - \text{Amount Found in Unspiked Sample}}{\text{Amount Spiked}} \times 100$$

(c) $$\text{Relative Percent Recovery} = \frac{\text{Percent Recovery from Waste Extract}}{\text{Percent Recovery from Tetraglyme Blank}} \times 100$$

(d) µg of Cl per 20 µL of extract

TABLE 27. REPEATABILITY OF POX DETERMINATIONS

Waste Sample	Amount of POX Found(a) in given Extract					
	Unspiked		Spiked at Low Level		Spiked at High Level	
	µg Cl/mL	% RSD(b)	µg Cl/mL	% RSD	µg Cl/mL	% RSD
Contaminated Soil	0.35	20	2.07	1	7.94	1
Latex Paint Waste	0.19	37	1.84	6	7.89	2
Ethanes Catalyst	2.31(c)	5	(d)	(d)	8.47(c)	6
Coal Gasif. Tar	2.99	5	(d)	(d)	10.50	4
Oxychlor. Catalyst	0.39	10	2.07	2	7.75	7
Treated POTW Sludge	2.30	12	(d)	(d)	9.24	7
Oil Refining Waste	0.35	37	2.01	6	7.95	2
Zimpro POTW Sludge	1.24	4	2.49	8	8.26	3
Wet POTW Sludge	0.17	35	1.70	5	7.15	1
Tetraglyme Blank	0.08	38	1.70	1	7.22	4

(a) Average of triplicate determinations.

(b) Percent relative standard deviation.

(c) µg Cl/20 µL

(d) Extracts were not spiked at the low level because of the relatively high level of POX found in the unspiked extract.

the extract volume analyzed was greater than 1 µg of Cl, the relative standard deviation was 8 percent or less. The relative standard deviation was considerably higher as the detection limit, 0.1 to 0.2 µg of Cl_2, was approached.

Tetraglyme blanks, a calibration standard, and a sodium chloride reference solution were analyzed several times each day for quality control purposes. The results obtained were very reproducible and are summarized in Table 28.

Varying volumes of a calibration solution containing 1,1,1-trichloroethane in tetraglyme were analyzed to determine the effect of spike level on the conversion efficiency. The results obtained are summarized in Table 29. The conversion efficiency was consistently 80 ± 5 percent over a range of 2 to 50 µg of chlorine. This conversion efficiency is essentially the same as the conversion efficiency (percent recovery) reported in Table 26 for the 12-component spiking solution.

TABLE 28. QUALITY CONTROL DATA FOR POX DETERMINATIONS

Sample	Number of Replicate Runs	Amount of POX Theor., µg/Cl	Amount of POX Found, µg/Cl	% RSD of Amount Found
Tetraglyme blank[a]	10	0.00	0.05	80
TCE calibration std.[b]	18	6.38	5.11	2
NaCl reference soln.[c]	12	5.00	5.37	5

(a) 1 mL of tetraglyme mixed with 7 mL or organic-free water and one drop of 10% Antifoam B emulsion.

(b) 25 µL of a tetraglyme solution containing 320 µg/mL of 1,1,1-trichloroethane mixed with 8 mL of organic-free water and one drop of 10% Antifoam B emulsion.

(c) 5 µL of an aqueous solution of NaCl containing 1 µg Cl/µL added directly to the titration cell.

TABLE 29. EFFICIENCY OF CONVERSION OF 1,1,1-TRICHLOROETHANE TO Cl^- IN POX DETERMINATION

Amount Injected,[a] µg of Cl	Amount Found,[b] µg of Cl	Conversion Efficiency, %[c]
2.55	2.03 ± 0.01	80
6.38	5.45 ± 0.04	85
12.75	10.38 ± 0.35	81
25.50	21.23 ± 0.15	83
51.00	39.72 ± 0.67	78

(a) The required amount of a tetraglyme solution containing 320 µg/mL of 1,1,1-trichloroethane was added to 7 mL of organic-free water.

(b) Average and standard deviation of duplicate determinations.

(c) Percent Conversion Efficiency = $\frac{\text{Amount Found}}{\text{Amount Injected}} \times 100$.

TASK 5. STUDY OF MATRIX EFFECTS ON DETERMINATION OF SEMIVOLATILE COMPOUNDS

INTRODUCTION

Methylene chloride extracts from nine unspiked wastes and methylene chloride blanks were analyzed by GC-FID and by a microcoulimetric TOX procedure with and without spiking with representative semivolatile compounds. This study was conducted to determine how much the total extractable matrix from the wastes affects the analytical results. A solvent exchange procedure for the removal of methylene chloride from the extracts was developed for use with the TOX analysis procedure.

EXPERIMENTAL

Extraction of Wastes

A 3.0-gram aliquot of unspiked waste was extracted with 150 mL of methylene chloride using the sonification procedure developed for the EMSL-Las Vegas interlaboratory study(8). A predetermined volume of the resulting extract was concentrated to 10.0 mL. The volumes selected for concentration and the concentration factors are given in Table 30. The values were selected on the basis of the GC-FID chromatograms of the extracts to give concentrates that would be as concentrated as possible without causing excessive interference in the GC-FID analysis. Whenever volumes greater than 100 mL were required, replicate aliquots were extracted and the extracts were combined. The 10-mL concentrates were used for both the TOX analyses and the GC-FID analyses.

Spiking of Concentrated Extracts

For the TOX analyses a 0.5-mL aliquot of each concentrate was spiked with 25 µL of an ethyl acetate solution containing 1 µg/µL of each of the six reference compounds listed in Table 31. The total halogen content of this spike solution was 2.57 µg Cl/µL. For the GC-FID analyses, two 1.0-mL aliquots of each concentrate were placed in 2-mL GC autosampler vials. One of the aliquots was spiked with 300 µL of a methylene chloride solution containing 50 µg of each of the 18 reference compounds listed in Table 32. The other aliquot was simply diluted by the addition of 300 µL of methylene choride. Several vials containing 1.0 mL of methylene chloride were spiked with 300 µL of the solution of reference compounds to provide calibration solutions.

TABLE 30. CONCENTRATION FACTORS APPLIED TO METHYLENE CHLORIDE EXTRACTS OF WASTES

Waste Sample	Volume of Extract Concentrated, mL	Concentration Factor
Contaminated Soil	100	10
Latex Paint	40	4
Ethanes Catalyst	20	2
Coal Gasif. Tar	2[a]	0.2
Oxychlor. Catalyst	1000	100
Treated POTW Sludge	200	20
Oil Refining Waste	10[b]	1
Zimpro POTW Sludge	100	10
NBS SRM-1645	350	35

(a) 2 mL was diluted to 10 mL.
(b) No concentration or dilution was required.

TABLE 31. COMPOUNDS SPIKED INTO METHYLENE CHLORIDE EXTRACTS OF WASTES TO BE ANALYZED FOR TOX

4-Chloroaniline	2,4-Dichloronitrobenzene
Bis(2-chloroethoxy)ethane	Pentachlorophenol
4-Chlorobenzoic acid	Hexachlorobenzene

TABLE 32. COMPOUNDS SPIKED INTO METHYLENE CHLORIDE EXTRACTS OF WASTES TO BE ANALYZED BY GC-FID

Benzaldehyde	2,4-Dinitrochlorobenzene
2,4,6-Trimethylpyridine	Pentachlorophenol
Nitrobenzene	Phenanthrene
2,4-Dimethylphenol	2,2',4,4'-Tetrachlorobiphenyl
4-Chloroaniline	4,4'-DDE
Bis(2-chloroethoxy)ethane	Diethylstilbestrol
4-Chlorobenzoic acid	Triphenyl phosphate
4-Methylquinoline	Chrysene
3-Nitroaniline	Bis(2-ethylhexyl) sebacate

Solvent Exchange

A 0.5-mL aliquot of the methylene chloride concentrate was transferred to a 15-mL tapered centrifuge tube which contained 5 mL of ethyl acetate. The tube was placed in a Vortex evaporator and concentrated to a volume of 0.5 to 0.8 mL at a temperature of 45°C. Another 5-mL aliquot of ethyl acetate was added and the sample was concentrated again to 0.5 mL. The sample was centrifuged to remove any suspended matter. The supernatant was carefully transferred to a 2.5-mL graduated centrifuge tube using a Pasteur pipet. The remaining particulate material was resuspended in 0.2 mL of tetraglyme and the sample was centrifuged again. The tetraglyme supernatant was added to the ethyl acetate supernatant. The particulate material was rinsed once again with tetraglyme in the same manner. The combined supernatants were made up to 1.0 mL with tetraglyme.

TOX Analysis

The TOX determination was performed using a Dohrmann MC-1/DX-20 instrument modified to enable syringe injections of sample extracts to be made. The modification involved replacing the usual TOX boat assembly with a ground glass socket joint sealed against the inlet of the pyrolysis tube on the Dohrmann and fitted with a Teflon-faced septum. Carbon dioxide and oxygen reagent gas lines were connected to separate external flow controllers which by-passed the existing gas controls. The CO_2 entered the pyrolysis tube at the normal fitting. The oxygen line was connected to a 16-gauge stainless steel needle which pierced the septum just below the center point, but within the inlet liner tube. The gas flows were 300 cc/min for CO_2 and 100 cc/min for O_2. All injections were made with a 100-µL syringe fitted with a removable 4-inch 26-gauge needle. Injections were made approximately in the center of the septum. All determinations were made in the POX mode of the instrument, starting the cycle before making an injection. The injection rate was approximately 1 µL/sec. Triplicate runs were made of each extract, a tetraglyme blank, a standard containing p-dichlorobenzene in tetraglyme (1.06 µg/µL or 0.5 µg/µL as Cl) and a titration cell check of 1 µg/µL NaCl in distilled water. Sample volumes were 50 µL for the extracts and blanks and 20 µL for the p-dichlorobenzene standard.

GC-FID Analysis

The following GC analysis conditions were used for the analysis of all samples:

Instrument:	Hewlett Packard Model 5730
Detector:	Flame ionization
Column:	30 m x 0.25 mm I.D. SE-52 glass capillary
Column Temp.:	60°C for 2 min; 60°C to 300°C at 8°C/min; 300°C for 16 min.

Injector Temp.:	300°C
Detector Temp.:	300°C
Injection:	2 µL splitless
Carrier Gas:	Hydrogen at 50 cm/sec at 25°C
Data Acquisition and Processing:	CIS-CALS computer system.

All samples were analyzed in triplicate. A calibration solution was analyzed before and after every six samples. All quantifications were based on peak areas using the external standard approach. The average of the peak areas obtained from the calibration runs conducted immediately before and after a sample set were used for the quantification of each resolvable compound in that sample set. The peak areas obtained in the calibration runs were used to calculate response factors for each compound relative to phenanthrene for quality control purposes.

RESULTS AND DISCUSSION

The results obtained for the TOX analyses are given in Table 33. The recoveries of TOX spiked into the waste extracts ranged from 87 to 99 percent were not significantly different from the recoveries of TOX in spiked blanks and spiked tetraglyme. It can be concluded that there are no significant matrix effects associated with the determination of the TOX content of waste extracts. The method is rapid and very reproducible. The low values obtained for unspiked blanks indicate that the solvent exchange procedure is quite effective.

The recoveries of all compounds except 4-chlorobenzoic acid spiked into the waste extracts and determined by GC-FID analysis are summarized in Table 34. The recovery of 4-chlorobenzoic acid was not determined because the GC column performance for this compound deteriorated too rapidly. In most cases the relative standard deviations were 15 percent or less, and the recoveries were between 85 and 115 percent indicating no significant matrix effects. However, in two cases very significant matrix effects occurred. In the case of the spiked extract from the ethanes catalyst, 2,4,6-trimethylpyridine and diethylstilbestrol were not detected at all above the background levels of the unspiked extract although many other compounds, including 2,4-dimethylphenol, were recovered quantitatively. The above results are clearly depicted in the gas chromatograms of the spiked extract and of the corresponding unspiked extract and calibration standard run immedately before and after the spiked extract, shown in Figures 1 and 2. In the case of the spiked extract from the oxychlorination catalyst, the recoveries of 2,4-dimethylphenol and 4-chloroaniline were severely depressed while many other compounds were recovered quantitatively and an enhanced peak was found for 4-chlorobenzoic acid. These results are depicted in Figure 3

TABLE 33. RECOVERY OF SEMIVOLATILE HALOGEN-CONTAINING ORGANIC COMPOUNDS FROM WASTE EXTRACTS BY TOX ANALYSIS

Sample	TOX Found, µg Cl/50 µL of extract[a]			
	Unspiked	Spiked[b]	Spiked Minus Unspiked[c]	Percent Recovery
Contaminated Soil	1.78(10)	7.24(2)	5.46	89
Latex Paint Waste	0.72(26)	6.11(1)	5.39	88
Ethanes Spent Catalyst	4.95(2)	10.61(3)	5.66	92
Coal Gasification Tar	0.97(16)	6.29(2)	5.32	87
Oxychlor. Spent Catalyst	1.24(3)	6.93(2)	5.69	93
Treated POTW Sludge	2.97(7)	8.46(4)	5.49	90
Oil refining Waste	0.75(7)	6.31(1)	5.56	91
Zimpro POTW Sludge	1.58(9)	7.56(1)	5.98	98
NBS SRM-1645	4.78(6)	10.82(2)	6.04	99
Blank A	0.42(7)	6.43(6)	6.01	98
Blank B	0.35(31)	5.94(3)	5.59	91
Tetraglyme[d]	0.21(29)	5.76(1)	5.55	91
QA Standard[d]	0.21(29)	8.52(8)[e]	8.31[f]	83

(a) Mean from triplicate analyses; percent relative standard deviation is given in parentheses.

(b) Mean has been corrected for the volume of spiking solution added to the extract.

(c) Theoretical value, except forthe p-dichlorobenzene QA standard, that would represent 100% recovery in 6.12 µg Cl/50 µL.

(d) The solvent exchange step was omitted.

(e) µg Cl/20 µL of standard.

(f) Theoretical value that would represent 100% recovery is 10.0 µg Cl/20 µL.

TABLE 34. RECOVERY OF SEMIVOLATILE ORGANIC COMPOUNDS FROM WASTE EXTRACTS DETERMINED BY GC-FID ANALYSIS

Compound	Percent Recovery (a) From Given Waste Extract								
	Contam. Soil	Latex Paint Waste	Ethanes Spent Catalyst	Coal Gasifcn. Tar	Oxychlor Spent Catalyst	Treated POTW Sludge	Oil Refining Waste	Zimpro POTW Sludge	NBS SRM#1645
Benzaldehyde	95(4)	(b)	85(5)	100(10)	95(10)	115(11)	95(7)	110(19)	92(8)
2,4,6-Trimethylpyridine	96(10)	(b)	(c)	106(15)	98(4)	109(17)	92(13)	91(18)	95(14)
Nitrobenzene	97(9)	(b)	99(2)	96(6)	99(5)	96(22)	92(8)	100(27)	92(8)
2,4-Dimethylphenol	97(9)	(b)	99(2)	116(11)	46(14)	112(14)	109(8)	110(29)	93(7)
4-Chloroaniline	92(7)	(b)	(b)	98(10)	64(7)	107(16)	104(15)	73(18)	87(10)
Bis(2-chloroethoxy)ethane	97(4)	97(6)	95(7)	95(13)	101(2)	112(14)	(b)	110(27)	96(16)
4-Methylquinoline	96(7)	106(4)	(b)	99(7)	104(4)	100(16)	(b)	(b)	99(1)
3-Nitroaniline	110(5)	107(5)	(b)	112(3)	(b)	(b)	(b)	94(21)	93(10)
2,4-Dinitrochlorobenzene	96(8)	101(3)	(b)	98(4)	(b)	89(21)	94(15)	80(10)	(b)
Pentachlorophenol	129(15)	103(9)	132(14)	111(7)	(b)	(b)	(b)	(b)	(b)
Phenanthrene	100(7)	95(6)	(b)	(b)	97(5)	106(10)	(b)	(b)	(b)
Tetrachlorobiphenyl	84(3)	95(2)	(b)	82(4)	99(2)	(b)	91(19)	(b)	(b)
4,4'-DDE	110(9)	89(9)	(b)	104(15)	(b)	91(14)	72(6)	93(30)	(b)
Diethylstilbestrol	(b)	85(9)	(c)	139(8)	79(19)	(b)	64(27)	(b)	(b)
Triphenyl phosphate	(b)	84(16)	99(9)	92(7)	104(6)	97(2)	76(22)	100(36)	(b)
Chrysene	(b)	85(13)	92(8)	84(9)	101(6)	99(11)	82(31)	99(20)	(b)
Bis(2-ethylhexyl)sebacate	(b)	90(11)	89(11)	94(6)	118(7)	110(9)	93(16)	110(33)	92(5)

(a) Average of triplicate GC runs; percent relative standard deviation is given in parentheses.

(b) Not determined because of interfering peaks.

(c) Not detected.

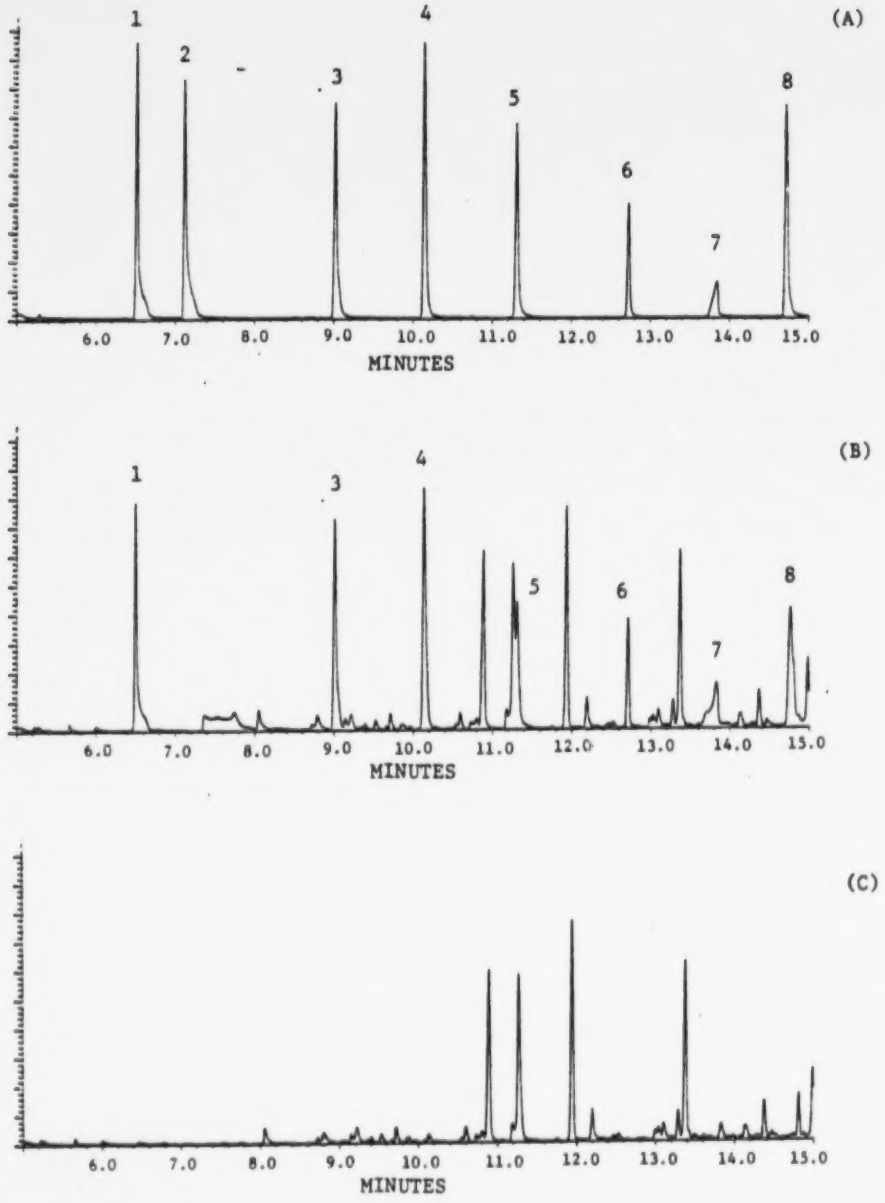

Figure 1. 5 to 15-Minute Section of GC-FID Chromatograms of (A) Calibration Standard, (B) Spiked Extract From Ethanes Catalyst, and (C) Unspiked Extract From Ethanes Catalyst. (1=Benzaldehyde, 2=2,4,6-Trimethylpyridine, 3=Nitrobenzene, 4=2,4-Dimethylphenol, 5=4-Chloroaniline, 6=Bis(2-chloroethoxy)ethane, 7=4-Chlorobenzoic acid, 8=4-Methylquinoline).

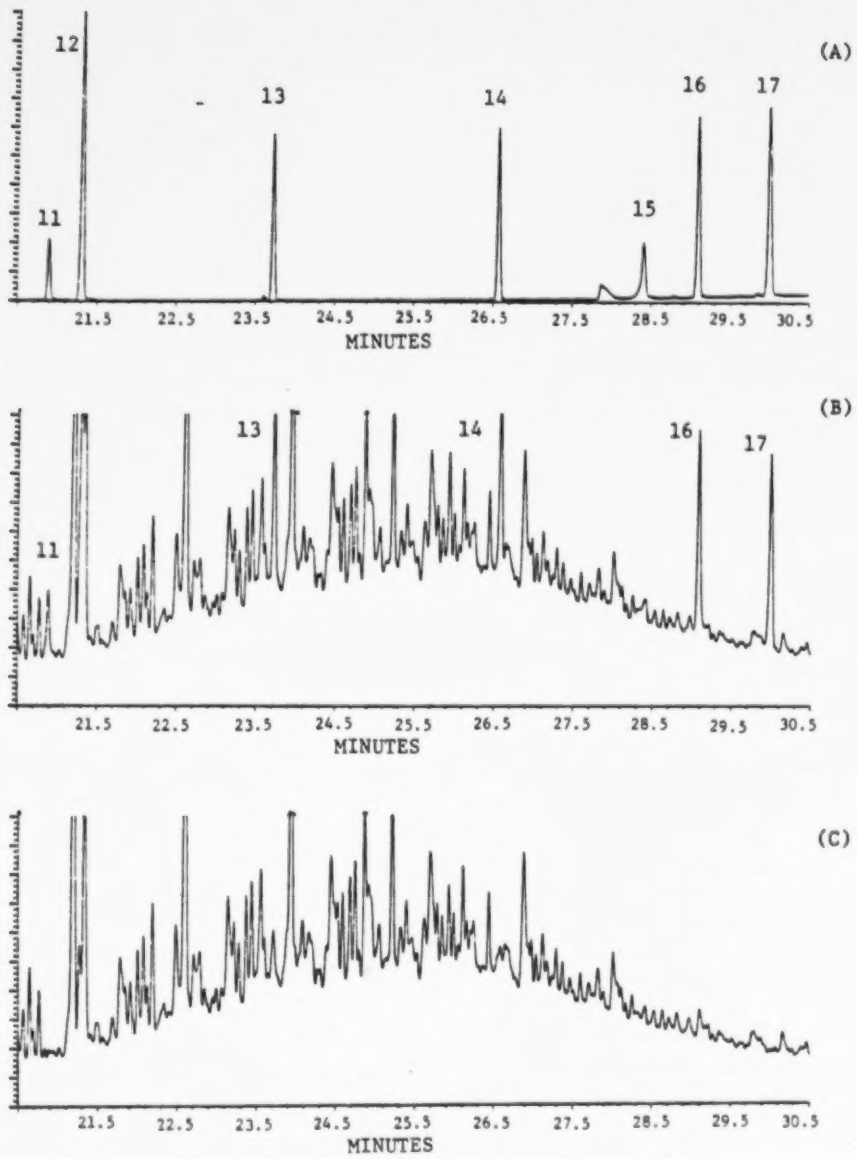

Figure 2. 20.5 to 30.5-Minute Section of GC-FID Chromatograms of (A) Calibration Standard, (B) Spiked Extract From Ethanes Catalyst, and (C) Unspiked Extract From Ethanes Catalyst. (11=Pentachlorophenol, 12=Phenanthrene, 13=Tetrachlorobiphenyl, 14=4,4'-DDE, 15-Diethylstilbestrol, 16=Triphenyl phosphate, 17=Chrysene.

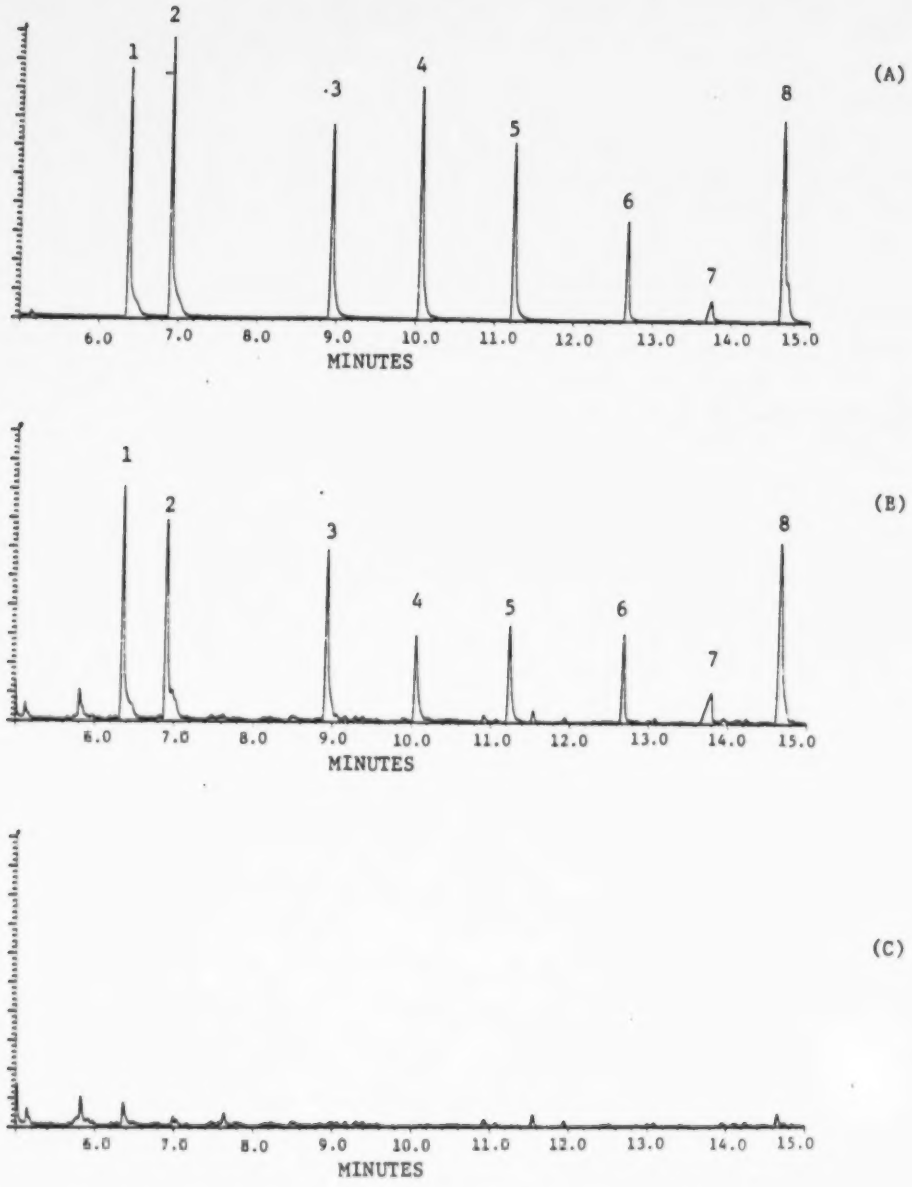

Figure 3. 5 to 15-Minute Section of GC-FID Chromatograms of (A) Calibration Standard, (B) Spiked Extract From Oxychlorination Catalyst, and (C) Unspiked Extract From Oxychlorination Catalyst. (1=Benzaldehyde, 2=2,4,6-Trimethylpyridine, 3=Nitrobenzene, 4=2,4-Dimethylphenol, 5=4-Chloroaniline, 6=Bis(2-chloroethoxy)ethane, 7=4-Chlorobenzoic acid, 8=4-Methylquinoline).

which shows the gas chromatograms of the spiked extract and of the corresponding unspiked extract and calibration standard run immediately before and after the spiked extract.

The above results demonstrate clearly that very significant matrix effects can occur in the GC analysis of waste extracts. The effects are both waste dependent and compound dependent. In some cases, a matrix effect may be caused by the physical interaction of a compound with coeluting material or by the selective entrapment of a compound by nonvolatile material that remains in the injection port. In other cases a matrix effect may be caused by chemical reactions that occur in the injection port or on the column between an individual compound and other extractable material. Another possible cause of a matrix effect is column deactivation by coeluting species to give an enhanced peak as probably happened in the cases of the enhanced peaks for pentachlorophenol in the ethanes catalyst extract and 4-chlorobenzoic acid in the oxychlorination catalyst extract. Because of the many possible causes, it is unlikely that matrix effects can be readily predicted. It is extremely important, however, that the likelihood of matrix effects in gas chromatographic work involving complex extracts be recognized, so that poor recoveries or inconsistent results are not automatically assumed to be caused by poor extraction efficiency, poor GC column performance or poor detector performance including poor mass spectrometer performance in the case of GC-MS analyses.

The presence of a matrix affect can best be detected by extensive quality control that includes the analysis of spiked extracts in addition to the analysis of samples spiked prior to extraction. Therefore, in all cases in which the reliability of analytical data is particularly critical, e.g. when the data are to be used for litigation purposes, it would seem prudent to conduct replicate analyses of unspiked samples, samples spiked at two or more levels, extracts spiked at two or more levels, and corresponding calibration solutions.

QUALITY ASSURANCE

The precision or repeatability of the TOX analyses is indicated by the percent relative standard deviations given in Table 33. When the amounts of TOX are 50 to 100 times greater than the detection limit, as in the cases of the spiked extracts, the precision was generally 1 to 5 percent which is excellent. The percent recovery, which is an indication of the conversion efficiency for converting organic chlorine to chloride, was generally 90 percent or greater for spiked waste extracts as well as for spiked blanks and spiked tetraglyme.

The precision or repeatability of the GC-FID analysis of spiked

extracts is indicated by the percent relative standard deviations given in Table 34. For the majority of the compounds determined, the relative standard deviation was 15 percent or less. However, for the compounds spiked into extracts of treated POTW sludge, oil refining waste, and Zimpro POTW sludge, the relative standard deviation was frequently 15 to 30 percent. The greater relative standard deviation is another indication of a matrix effect.

The GC performance was monitored by analyzing a calibration solution prior to any sample analyses and after the analysis of every six samples. The response factors for all compounds relative to phenanthrene were recorded for each calibration run. Whenever the response factor for any one component, except diethylstilbestrol, decreased to a value below 75 percent of the original value, indicating excessive column deterioration had occurred, 25 cm of the injector end of the GC column was removed or the column was replaced by a new column. The data obtained from the six samples analyzed just prior to a calibration run that indicated column deterioration, were discarded; and the samples were reanalyzed. Thus the only sample analysis data considered acceptable were those obtained from sample analysis runs that were bracketed by acceptable calibration runs. The data summarized in Table 34 include data from four sets of analyses. The first set of data was obtained using a new GC column, the second set was obtained after the end of the column was removed, the third set was obtained using a second new column, and the fourth set was obtained after the end of the second column was removed. The average response factors and corresponding relative standard deviations obtained from the calibration runs associated with each set of analyses are given in Table 35. The absolute area responses for the phenanthrene internal standard are also included in the table. The relative standard deviations of the response factors of all of the compounds except pentachlorophenol and diethylstilbestrol were usually less than 10 percent. The higher standard deviations obtained from pentachlorophenol and diethylstilbestrol indicates that the column performance for these particular compounds was modified by the injection of extracts. The relative standard deviation of the peak area of phenanthrene was also usually less than 10 percent, which indicates that the external standard approach used for quantification was reliable.

TABLE 35. RESPONSE FACTORS OBTAINED FROM CALIBRATION RUNS

Compound	Response Factor[a][b] From Given Set of Analyses			
	Set 1[c]	Set 2[d]	Set 3[c]	Set 4[d]
Benzaldehyde	1.14(3)	1.23(3)	1.16(8)	1.27(5)
2,4,6-Trimethylpyridine	1.04(4)	1.13(5)	1.09(8)	1.17(3)
Nitrobenzene	1.36(2)	1.49(5)	1.40(8)	1.53(5)
2,4-Dimethylphenol	1.10(2)	1.19(5)	1.16(7)	1.24(6)
4-Chloroaniline	1.53(2)	1.75(5)	1.60(11)	1.70(5)
Bis(2-chloroethoxy)ethane	3.11(2)	3.69(7)	3.18(8)	3.63(4)
4-Methylquinoline	1.21(8)	1.25(9)	1.19(16)	1.22(8)
3-Nitroaniline	2.20(4)	2.57(6)	2.18(7)	2.29(4)
2,4-Dinitrochlorobenzene	3.15(8)	3.68(7)	3.21(4)	3.44(3)
Pentachlorophenol	5.05(12)	6.44(15)	5.08(11)	5.28(5)
Tetrachlorobiphenyl	1.95(1)	1.87(3)	1.90(2)	1.90(3)
4,4'-DDE	1.84(2)	1.73(3)	1.79(4)	1.85(4)
Diethylstilbestrol	5.53(53)	3.35(13)	3.65(25)	3.60(32)
Triphenyl phosphate	1.56(6)	1.50(7)	1.53(2)	1.56(6)
Chrysene	1.31(6)	1.29(6)	1.24(1)	1.29(7)
Bis(2-ethylhexyl) sebacate	1.89(7)	1.75(8)	1.79(2)	2.02(17)
Phenanthrene (Peak Area)	76.3(5)	72.8(9)	88.5(13)	96.0(5)

(a) Response factors given were calculated by a CIS-CALS data system as the area of phenanthrene internal standard divided by the area of the listed compound at the same concentration and are thus the inverse of response factors calculated in the usual manner.

(b) Percent relative standard deviation is given in parentheses.

(c) Average of three replicates.

(d) Average of four replicates.

TASK 6. COMPARISON OF ANALYSIS METHODS FOR DETERMINING PURGEABLE COMPOUNDS

INTRODUCTION

The determination of purgeable organic compounds in aqueous leachates and tetraglyme extracts of solid wastes is normally performed by GC-MS analysis which generally provides confirmatory qualitative information as well as quantitative information. However, there are other analysis methods, e.g. GC-PID/Hall analysis and POX analysis, which are considerably less costly than GC-MS analysis and which may be very useful for screening large numbers of samples. Task 6 was undertaken to determine how closely data obtained from GC-PID/Hall analysis and POX analysis agree with data obtained from GC-MS analysis.

EXPERIMENTAL

Aqueous leachates and tetraglyme extracts of two solid waste samples were analyzed in triplicate by GC-MS, GC-PID/Hall, and POX analysis procedures. The two solid wastes were a spiked latex paint waste, ILS-2, and a spiked ethanes spent catalyst, ILS-3.

The aqueous leachates were prepared by placing 8 g of waste in a 250-mL centrifuge tube, adding 160 mL of water, capping the tube with a Teflon-lined screw cap, tumbling the sample end over end for 24 hours, and centrifuging for 10 minutes at 2500 rpm. The supernatant was poured into three 40-mL vials which were sealed using screw caps fitted with Teflon-faced septa. The vials were filled completely full with no air space and placed in an inverted position in a one-quart paint can having a tightly-fitting lid. The can containing the samples was placed in a one-gallon paint can containing activated carbon and stored at 0-5°C until use.

The tetraglyme extracts were prepared as described for Task 4. The GC-MS analyses were conducted as described for Task 2-1; the GC-PID/Hall analyses and the POX analyses were conducted as described for Task 4.

RESULTS AND DISCUSSION

The amounts of individual purgeable compounds found in the leachates by GC-PID/Hall and GC-MS analysis are given in Table 36. The amounts found in the tetraglyme extracts are given in Table 37. The total purgeable halogen contents of the individual compounds found by GC-Hall and GC-MS were calculated and are presented in Table 38 along with the results from the POX analyses.

TABLE 36. COMPARISON OF GC-PID/HALL AND GC-MS FOR DETERMINATION OF PURGEABLE COMPOUNDS IN LEACHATES

Compound	Amount Found[a], µg/mL (% RSD), in Leachate from ILS-2 by Given Method		Amount Found[a], µg/mL (% RSD) in Leachate from ILS-3 by Given Method	
	GC-PID/Hall[b]	GC-MS	GC-PID/Hall[b]	GC-MS
Propionitrile	ND[c]	7.6 (5)	ND	24 (4)
1,1-Dichloroethylene	ND	0.58 (8)	ND	3.4 (8)
trans-1,2-Dichloroethylene	ND	ND	22 (1)	23 (1)
1,1-Dichloroethane	1.6 (18)	3.0 (1)	430 (2)	970 (1)
Chloroform	ND	ND	6.9 (4)	5.7 (2)
2-Chloroacrylonitrile	10 (10)	16 (4)	11 (4)	7.0 (1)
1,1,1-Trichloroethane	8.4 (22)	14 (2)	28 (8)	47 (8)
Carbon tetrachloride	(d)	4.0 (2)	(d)	14 (6)
1,2-Dichloropropane	4.3 (9)	4.5 (2)	30 (3)	27 (2)
Trichloroethylene	1.0 (13)	1.4 (3)	ND	ND
Bromoform	20 (4)	29 (7)	11 (1)	12 (8)
2-Hexanone	17 (4)	37 (5)	ND	9.9 (1)
1,1,2,2-Tetrachloroethane	2.4 (5)	2.2 (5)	4.9 (7)	3.7 (3)
Tetrachloroethylene	(e)	0.41 (2)	(e)	ND
Chlorobenzene	1.9 (9)	2.5 (3)	0.8 (13)	1.5 (2)
Ethylbenzene	7.0 (8)	13 (1)	ND	2.4 (3)
o-Xylene	8.8 (5)	12 (2)	ND	ND

(a) Average of triplicate determinations.

(b) All halogen-containing compounds were determined using a Hall detector; all other compounds were determined using a photoionization detector.

(c) Not detected.

(d) Coeluted with 1,1,1-trichloroethane; any carbon tetrachloride obtained is included in the amount reported for 1,1,1-trichloroethane.

(e) Coeluted with 1,1,2,2-tetrachloroethane; any tetrachloroethylene obtained is included in the amount reported for 1,1,2,2-tetrachloroethane.

TABLE 37. COMPARISON OF GC-PID/HALL AND GC-MS FOR DETERMINATION OF PURGEABLE COMPOUNDS IN TETRAGLYME EXTRACTS

Compound	Amount Found[a], µg/mL (% RSD), in Extract from ILS-2 by Given Method		Amount Found[a], µg/mL (% RSD), in Extract from ILS-3 by Given Method	
	GC-PID/Hall[b]	GC-MS	GC-PID/Hall[b]	GC-MS
Propionitrile	ND[c]	9.1 (13)	ND	22 (12)
1,1-Dichloroethylene	ND	ND	ND	23 (14)
trans-1,2-Dichloroethylene	ND	ND	74 (10)	85 (9)
1,1-Dichloroethane	ND	ND	340 (5)	2200 (5)
Chloroform	ND	ND	37 (5)	22 (5)
2-Chloroacrylonitrile	13 (2)	24 (9)	49 (11)	44 (6)
1,1,1-Trichloroethane	29 (5)	39 (5)	250 (5)	560 (6)
Carbon tetrachloride	(d)	12 (6)	(d)	160 (6)
1,2-Dichloropropane	7.8 (4)	7.4 (5)	130 (6)	120 (4)
Trichloroethylene	2.6 (10)	2.3 (3)	ND	ND
Bromoform	42 (1)	58 (8)	85 (15)	110 (10)
2-Hexanone	26 (5)	33 (13)	ND	15 (18)
1,1,2,2-Tetrachloroethane	12 (6)	9.4 (5)	41 (21)	32 (6)
Tetrachloroethylene	(e)	6.6 (3)	(e)	ND
Chlorobenzene	9.8 (7)	11 (2)	40 (13)	31 (3)
Ethylbenzene	61 (7)	100 (4)	89 (9)	130 (12)
o-Xylene	79 (4)	97 (1)	ND	ND

(a) Average of triplicate determinations.

(b) All halogen-containing compounds were determined using a Hall detector; all other compounds were determined using a photoionization detector.

(c) Not detected.

(d) Coeluted with 1,1,1-trichloroethane; any carbon tetrachloride obtained is included in the amount reported for 1,1,1-trichloroethane.

(e) Coeluted with 1,1,2,2-tetrachloroethane; any tetrachloroethylene obtained is included in the amount reported for 1,1,2,2-tetrachloroethane.

TABLE 38. COMPARISON OF POX, GC-HALL AND GC-MS FOR DETERMINATION OF PURGEABLE HALOGEN COMPOUNDS IN LEACHATES AND TETRAGLYME EXTRACTS

Sample	Amount of Purgeable Organic Halogen,[(a)] µg Cl/mL (% RSD), Obtained Using Given Analytical Method		
	POX	GC-Hall	GC-MS
Latex Paint Waste, ILS-2			
Leachate	30 (7)	26 (10)	43 (4)
Tetraglyme extract	71 (6)	66 (4)	100 (7)
Ethanes Spent Catalyst, ILS-3			
Leachate	490 (10)	370 (2)	800 (1)
Tetraglyme extract	2500 (2)	710 (6)	2500 (6)

(a) Average of triplicate determinations; calculated as organic chlorine in which a mole of bromine is considered as a mole of chlorine.

The agreement found among the three analytical methods was considered very good. In most cases the amounts of the total organic halogen found by the three methods were within a factor of two from each other. The amounts of individual compounds found by the GC-PID/Hall analyses were generally within a factor of two of those found by GC-MS analysis. An example of chromatograms obtained from the GC-PID/Hall analysis of a leachate is given in Figure 4.

The results indicate that the POX analysis method can be very effective as a rapid and inexpensive procedure for screening aqueous leachates and tetraglyme extracts obtained from solid wastes. When the quantification of individual components is required, the GC-PID/Hall analysis method can often be used instead of a more costly GC-MS method. However, when two components coelute from the GC column, as in the case of 1,1,2,2-tetrachloroethane and tetrachloroethylene, GC-MS is required for identification and quantification of the two components.

QUALITY ASSURANCE

The reproducibilities of the GC-PID/Hall analyses and POX analyses for this task are indicated by the percent relative standard deviations reported in Tables 36, 37, and 38. In most cases the relative standard deviations were less than 10 percent.

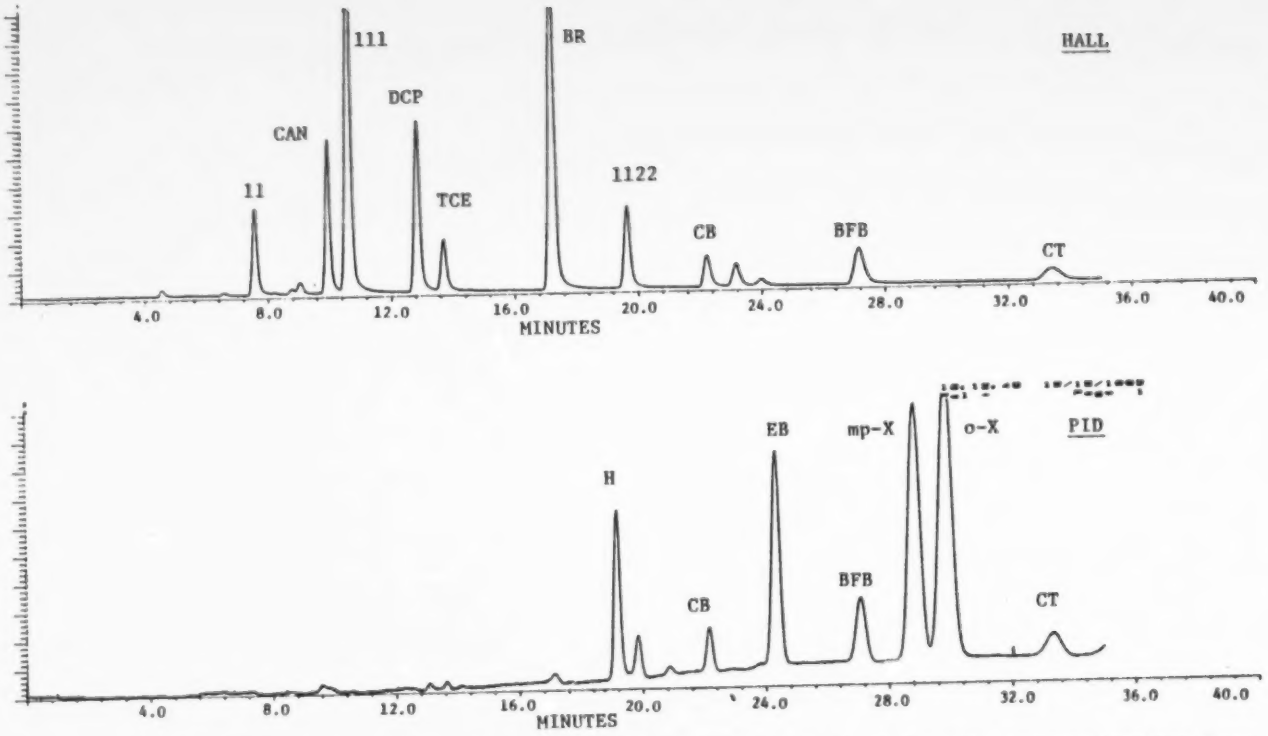

Figure 4. GC-PID/Hall Chromatograms of the Purgeable Components Obtained From the Aqueous Leachate From a Spiked Latex Paint Waste. (11=1,1-Dichloroethane; CAN=2-Chloroacrylonitrile; 111=1,1,1-Trichloroethane; DCP=1,2-Dichloropropane; TCE=Trichloroethylene; BR=Bromoform; 1122=1,1,2,2-Tetrachloroethane; CB=Chlorobenzene; BFB=4-Bromofluorobenzene; CT=4-Chlorotoluene, H=2-Hexanone; EB=Ethylbenzene; mp-X=m&p-Xylene; o-X=o-Xylene).

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